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THE CHEMICAL COLORING OF METALS

THE CHEMICAL COLORING OF METALS

AND ALLIED PROCESSES

BY

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PREFACE

THE subject of metal coloring is not unduly represented in the technical press. Few works have so far appeared.

It was therefore thought by the authors that, in view of the wide extension of metal manufactures, and of the numerous applications of metals and the need for protection and the desire for decorative effects, a simple treatise on the subject would be acceptable.

It is, however, not for one moment to be imagined that the subject is one which can be fully treated in, or grasped from, a book. Metal coloring is an art; indeed, it is a fine art. Success depends upon the realisation of a number of conditions.

The craftsman must at least be acquainted with the properties of the metals which he handles, and the materials by means of which he proposes to attain the desired result. Thus a simple outline of the chemistry of some of these materials is considered to be inevitable to ensure their intelligent use. These preliminary chapters are intended to serve as a stimulus to a wider chemical knowledge which will constitute a *sine qua non* in striking out upon new lines.

Manipulative skill is no less important. Some of these metal-coloring processes are designed to effect in a few minutes the changes which, in ancient metals, have occupied decades or even centuries. The present modern rapid methods will therefore demand a quick perception

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of the desired effects, and an equally speedy manipulation, to prevent them from being carried beyond the desired point.

Finally, the artistic temperament will be required to attain results which will be regarded as best in harmony with the final setting of the work.

Even given these essentials, any text-book can only indicate possibilities, and must not be regarded as the omega of the subject.

Practical directions are necessarily brief, and the personal element of the operator must come largely into play. In all cases of practical work, such artistic processes defy accurate description. There is also frequently some room for elasticity in the several operations, and the guidance of a skilled operator is invaluable.

With these brief observations the authors commend the book to their readers, and acknowledge with gratitude their indebtedness to Messrs. W. Canning and Co., Ltd., Messrs. Grauer and Weil, Ltd., and Messrs. Cassell and Co., Ltd., for the loan of the blocks of the illustrations.

S. F.
S. R. B.

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INTRODUCTION

Even a cursory glance at many of the metallic works of art to be found in the world's museums, at once excites the admiration of those who do not profess even initiation into the realm of the artistic.

From the earliest history of man his manipulative skill became exercised in the art of adapting materials in the production of tools serviceable to his daily needs. The flint tools are the relics of the Stone Age, and as they are turned up by the archæologist we behold them in much the same form and appearance as when they were laid down by their users. Flint is a form of silica which, as the chemist well knows, is age-enduring, suffering little or no alteration under the conditions to which it is likely to be exposed.

Soon, however, we pass from the Stone Age to the Bronze Age. Some of the early metals which then came into use were found as such in nature; others were later obtained by some simple furnace treatment which usually involved heating in a fire, or, as the metallurgist would now say, in a reducing atmosphere. The metal-bearing materials were frequently by no means pure. Such complex minerals, or ores as we now call them, being impure could only yield metals which, too, were not simple in composition. These mixtures of metals or alloys were discerned to have properties which combined the essentials of workability and suitability for the

production of tools. Thus in the Bronze Age the predominating metal is an alloy with copper as its chief constituent, and containing varying proportions of other metals, such as tin and zinc. Many of the ancient bronzes correspond approximately to those so styled to-day. Other examples, however, more nearly corresponded to the alloy which we now call brass. As a matter of fact, the terms brasses and bronzes were used in an elastic manner regardless almost of composition.

Recently scientific minds have given some attention to the subject of nomenclature. To-day bronzes are alloys containing a large proportion of copper, the second constituent being mainly tin. Thus :—

Gun metal . . .	90 copper, 10 tin.
Bell metal . . .	80 ,, 20 ,,
Speculum metal . .	66 ,, 34 ,,

are bronzes. So also is :—

Coinage bronze . .	95 copper, 4 tin, 1 zinc.

Similarly the brasses are copper alloys with zinc as the second chief constituent. Thus :—

Gilding metal . .	80 copper, 20 zinc.
Cartridge brass . .	70 ,, 30 ,,
Admiralty brass . .	70 ,, 28 ,, 2 tin

conform to this definition.

Similar alloys, but of less definite composition than is now the rule, were at one time in extensive use, and gave rise to the recognised Bronze Age.

These alloys embodied properties which admitted of the impression of the manipulative skill of the craftsman. They could be easily fashioned into desired shapes and

would receive the sharp edges which could be renewed from time to time, and, moreover, admitted of elaborate decoration in the hands of the skilled engraver. These were the days when no labour was too much to devote to a single work of art.

The ancient works of metallic art included many war implements, domestic appliances and heraldic emblems. Spears, knives, axes, cauldrons, bells, horns, lamps, bowls, clocks and candlesticks are but a few examples of many which have from time to time been brought to light. They have been raised by the agriculturist's plough or have been excavated by the archæologist from almost every corner of the world. They cover vastly separated periods in human history, and each throws some light upon the manners and customs of their times.

Examples of more recent origin can be displayed in a correct setting, and many old mansions which now serve as museums give to such metal curios their correct setting. One very good illustration may be seen in a seventh-century room which has been admirably arranged in the London Museum at Stafford House. Examples of metal art ware are here found in what we may regard as somewhat of their original setting, and armour and breastplates, candlestick and mortar, bedwarmer and trivet, and smaller examples are found in an interesting and instructive arrangement. Other very good illustrations of the heavy brass and copper ware which served so long ago are to be found in many continental cities, and provide a striking contrast with the clean light aluminium ware which characterises the modern kitchen.

Colors Produced by Age.—One striking difference between those times and to-day is found in the present

excessive use of metal polishes. In the average household of to-day the intricate design on much metal work is largely worn out by undue polishing. While something may be said for brightness and cleanliness, yet we, in other directions, distinctly avoid excessive lustre.

By exposure to air most metals soon acquired a tint or patina which became more or less permanent. Some form of superficial action occurred, in time imparting a very pleasing and artistic effect. To apply our modern methods of cleaning and polishing would indeed be an act of vandalism in the eye of the collector of such curios. The methods of cleaning which may be adopted are of a very gentle nature, intended to preserve the tints which have been slowly acquired during the early service and exposure.

What we rather aim at to-day is to impart to new metal work some appearance of age.

It may be difficult to trace any definite origin to the modern methods of metal coloring. It is well known that in France the art of bronzing early developed, but "up to year 1828 only one color of bronze was known to the trade, and this was verde antique of different shades according to the taste of the customer." In this year the Florentine bronze of "Bronze Lafluer" (named after the artist) began to appear, and a few job shops were established to do bronzing for the trade. This was the beginning of the art of bronzing.

After the Florentine bronze came the Florentine fume or smoked Florentine bronze, M. Camus being the first to produce it in 1833. Next came the "verde artistique," a pale green, relieved on the high lights with yellow bronze powder. This was followed by "bronze médaille," or

medal bronze. M. Masselotte was the best artist of this period and was renowned for his peculiar and artistic finishes. Later there appeared the "bronze fer," or iron-bronze, which was followed by the smoked bronzes introduced by M. Lemoine, and which are, even to-day, recognised as some of the best finishes known to the art. This work was produced on only very expensive bronzes. M. Barbedienne was the originator of a color of bronze still bearing his name and in extensive use to-day.

From 1870 up to the present time scores of painted bronzes have made their appearance. These finishes are produced by mixing fine colors ground in poppy oil, mixed with bronze powders and a special varnish known as French mission. The figures are first brass plated and then oxidised with a mixture of oxide of iron and graphite. When the figures are dry, the bases, the draperies and sometimes the hair are painted black and the flesh a lighter color. In some figures five or six coats are necessary to produce the desired tone. After each coat they are rubbed down with water and rottonstone, and, when finished, they have the appearance of a piece of solid bronze, owing to the bronze powder incorporated into the pigments. The coating is perfect when it is impossible to scratch the finish with the thumb nail.

THE CHEMICAL COLORING OF METALS

CHAPTER I

CHEMISTRY

Introduction.—A somewhat close acquaintance with the chief chemical substances which are concerned with metal coloring processes now becomes necessary. A simple knowledge of chemistry is an essential to the intelligent use of materials commonly called chemicals. Ignorance is often disastrous. A brief examination of air reveals the existence of several kinds of materials with destructive properties. Throughout the work which follows we shall meet very many more. Some are very simple in their composition, while many are very complex.

Elements.—An exhaustive examination of all kinds of materials reveals the existence of some ninety quite different kinds of simple substances. These are called *elements*. They are chiefly solid at ordinary temperature. Two, mercury and bromine, are liquid, while a few, including oxygen, hydrogen, nitrogen, and chlorine, are gaseous. These elements may be looked upon as the fundamental materials, which either separately, or variously combined provide all known terrestrial materials.

Chemical Compounds.—These elements sometimes occur free in nature. More often they are united together in various but very definite proportions, producing substances of totally different properties. These more complex bodies are called *chemical compounds*. One important feature about them is their very definite composition. Using approximate figures, pure water always contains just hydrogen and oxygen in the proportion of 1 : 8 by weight. Carbonic acid gas always contains carbon and oxygen in the proportion of 3 : 8, while cane sugar contains carbon, hydrogen and oxygen in the proportions of 72 : 11 : 88. Constant composition is the rule of chemical compounds. There would appear to be no limit to the number of possible compounds. Thousands are known—intimately—while new ones are always coming to light. The possibilities of the existence of such enormous numbers may be appreciated when it is recalled that from merely twenty-six letters of the alphabet there would appear to be no limit to the number of words (made by compounding the few letters in different numbers and arrangements), each word embodying some definite thought. Similarly each compound possesses certain characteristic properties. By these they are recognised. Chemical analysis is a searching after properties which characterise different substances. Usually the properties of a compound are so totally different from those of its constituent elements as to afford no indication of their presence. Water, for instance, gives no obvious hint that it contains hydrogen and oxygen. It is similarly difficult to realise that sugar is made up of its constituents which have already been mentioned.

Mixtures.—Now it is further possible to conceive that

elements might be merely mixed together without any trace of combination. Iron filings and sulphur, for example, may be mixed in any proportion. This mixture is heavy or light, and dark or yellow, according to the proportions of the two substances present. The mixtures share the properties of the elements, and the constituent elements may be separated by some simple process. Thus from the mixture of iron filings and sulphur a magnet will attract out most or all of the iron, while from a mixture of two compounds, sand and sugar, the latter may be readily dissolved out by means of water. Such mixtures are totally different from chemical compounds.

Chemical Symbols.—For purposes which will soon be clearly seen, the elements have received from chemists a brief designation called "*symbols.*" These symbols consist of either one or two letters, generally the most prominent ones in the name or the Latin equivalent. Thus iron (ferrum) is represented by Fe, copper (cuprum) by Cu and silver (argentum) by Ag. At present we will attach to them merely a qualitative meaning. They represent different kinds of simple matter. They are samples of the chemist's shorthand. Later, it will be necessary to regard these symbols as expressions of relative quantities of the elements for which they stand.

Molecules and Atoms.—Some idea of the extent of the divisibility of matter may be gained by finely grinding a lump of sugar. The particles will be so small as to be individually invisible to the naked eye. Permanganate of potash may be similarly ground. The merest small particle of the permanganate, when added to water, pro-

duces a very obvious color throughout the liquid. Where there is color there is permanganate. This carries the divisibility of matter to an extreme limit. We must imagine the tiny particles of permanganate in the solution which neither the eye nor a microscope can individually see. They represent limits of division of the permanganate. These smallest parts, capable of a separate existence and retaining the characteristic properties of the compound, are called *molecules*. So small are they that the late Lord Kelvin stated that if a drop of water were magnified to the size of the earth, then with the same magnification, molecules would vary in size from marbles to cricket balls. Again, further dilution of the solution merely serves to further separate the molecules of dissolved sugar. A good deal of information about the dimensions of these molecules is available but does not concern us here.

Sugar, however, is a chemical compound. It contains three elements: carbon, hydrogen and oxygen. Then each molecule of sugar must also contain still smaller parts of these elements. These smaller parts are called *atoms*. When these atoms are separated the compound loses its characteristic properties. The sugar ceases to be sugar. The molecule is thus the smallest part of a chemical compound, while the atom is the smallest part of an element. In the molecule of a compound the atoms are not all alike. The elements, however, also have molecules, in which all the atoms are alike. This is all of considerable interest and importance to us, inasmuch as when chemical compounds change their properties they do so most usually by a change of composition. These changes occur in individual molecules. We observe the

sum total of such molecular changes. Our metal coloring reactions take place not directly between masses of materials, but between their molecules and even atoms.

Atomic Weights.—Going a step further, it has now to be stated that, by a long series of investigations carried on with the greatest accuracy by many experimenters, the relative weights of the atoms have been obtained. It is quite unnecessary here to even outline the methods of such determinations ; their use is of more value to us. In fixing these relative numbers, some standard was required. For reasons which need not now be adduced, oxygen has been selected and fixed as 16. The relative weights of atoms to this standard are called *atomic weights*. Thus if 16 is taken as the weight of an atom of oxygen then that of copper is 63·6. The atom of copper is nearly four times as heavy as that of oxygen.

Here it may be advisable to draw attention to the difference between atomic weights and specific gravities. An element with a high atomic weight is not necessarily heavy. To take an example, the atomic weight of lead is 207 and its density 11·4, while the atomic weight of gold is 197 and its density 19·5. Many other similar cases can be observed and are worth a little consideration. The simple explanation of the apparent anomaly is that atomic weights are relative weights of individual atoms, quite independently of their size, while densities represent relative weights of equal volumes, and we can therefore readily picture a cubic centimetre of gold containing many more atoms than a cubic inch of lead. The density of a metal is subject to small variations according to the treatment of the metal. The atomic weight is, however, constant.

The following table embodies a number of the more important elements :—

Element.	Symbol.	Metal (M) or Non-metal (N).	Atomic weight.
Aluminium	Al	M	27
Antimony	Sb	M	122
Arsenic	As	?	75
Barium	Ba	M	137
Bismuth	Bi	M	208
Boron	B	N	11
Bromine	Br	N	80
Cadmium	Cd	M	112
Calcium	Ca	M	40
Carbon	C	N	12
Chlorine	Cl	N	35·5
Chromium	Cr	M	52·5
Cobalt	Co	M	59
Copper	Cu	M	63·6
Fluorine	F	N	19
Gold	Au	M	197
Hydrogen	H	?	1
Iodine	I	N	127
Iron	Fe	M	56
Lead	Pb	M	207
Magnesium	Mg	M	24
Manganese	Mn	M	55
Mercury	Hg	M	200
Nickel	Ni	M	58·6
Nitrogen	N	N	14
Oxygen	O	N	16
Phosphorus	P	N	31
Platinum	Pt	M	195
Potassium	K	M	39
Silicon	Si	N	28
Silver	Ag	M	108
Sodium	Na	M	23
Strontium	Sr	M	87·6
Sulphur	S	N	32
Tin	Sn	M	118
Zinc	Zn	M	65

Properties of Common Elements.—We now give a list of the more common elements with a few characteristic properties :—

Aluminium. Al. At. wt. 27.—A brilliant white metal ; malleable, ductile and valuable on account of its lightness combined with strength, its electrical conductivity and its general resistance to rapid corrosion.

Antimony. Sb. At. wt. 122.—A bluish white, heavy, crystalline metal ; brittle and used chiefly for hardening lead, as in bullet metal and printers' alloys.

Arsenic. As. At. wt. 75.—A brittle steel-grey solid. Its compounds are extremely poisonous.

Bismuth. Bi. At. wt. 208.—A lustrous white and crystalline metal with a faint reddish tinge. It melts at 268° C. Density 9·8 ; it is not a very good conductor of electricity.

Bromine. Br. At. wt. 80.—A dark red non-metallic liquid, volatile and producing a dark red vapour even at ordinary temperature.

Calcium. Ca. At. wt. 40.—An essential constituent of all lime and chalk. It is difficult to isolate, and is not much used in the free form.

Carbon. C. At. wt. 12.—Occurs in many impure forms as charcoal, coke, graphite, lampblack and diamond. Produces carbonic acid gas when burned in air or in oxygen.

Chlorine. Cl. At. wt. 35·5.—A greenish yellow gas of suffocating odour. Present in hydrochloric acid and salt.

Cobalt. Co. At. wt. 59.—A grey metal, resembling nickel but produces many red compounds. Cobalt is now being deposited as an improved substitute for nickel.

Copper. Cu. At. wt. 63·6.—A fairly heavy metal with

characteristic red color. Density 8·92, melting-point 1100° C. Malleable and ductile; excellent conductor of electricity.

Gold. Au. At. wt. 197.—A yellow, heavy yet soft metal, exceedingly malleable and ductile. Density 19·5; melting-point 1050° C. Chemically inert and therefore only slightly corroded except under special circumstances.

Hydrogen. H. At. wt. 1.—A light, odourless, inflammable gas. Constitutes $\frac{1}{9}$ of the weight of water and forms very explosive mixtures with air or oxygen. An essential constituent of all acids.

Iodine. I. At. wt. 127.—A lustrous deep violet crystalline solid. Easily volatilised without liquefying and yields a dark violet vapour.

Iron. Fe. At. wt. 56.—Properties well known.

Lead. Pb. At. wt. 207.—A soft but heavy metal; density 11·4; bluish color.

Magnesium. Mg. At. wt. 24.—A nearly white malleable metal; very light, density 1·6. Burns with a brilliant flame producing magnesia.

Manganese. Mn. At. wt. 55.—A dark steel-grey brittle metal largely used in steel manufacture.

Mercury. Hg. At. wt. 200.—The only metal liquid at ordinary temperature. Density 13·6; commonly known as quicksilver. Permanent in air.

Nitrogen. N. At. wt. 14.—Well known.

Oxygen. O. At. wt. 16.—Well known.

Phosphorus. P. At. wt. 31.—A yellow waxy solid, easily ignited and hence used in the manufacture of matches. Kept under water to prevent self-ignition. Present in substances called phosphates.

Platinum. Pt. At. wt. 195.—A silvery malleable and

ductile metal characterised by its high density, non-corrodibility and high melting-point.

Potassium. K. At. wt. 39.—A violet and light metal, lustrous when freshly cut, but tarnishes rapidly. Burns when placed in water, producing caustic potash. Hence usually kept under naphtha.

Silver. Ag. At. wt. 108.—A white, malleable and ductile metal. Not easily attacked by acids in foods, hence its use in tableware. Tarnishes in air by action of certain sulphur compounds. Equals or excels copper in electrical conducting power.

Sodium. Na. At. wt. 23.—A very light, soft and yellow metal. Lustrous when freshly cut, but rapidly tarnishes. Burns when placed in water, forming caustic soda. Occurs in common salt.

Sulphur. S. At. wt. 32.—Brittle yellow non-metal, burning with a pale blue flame, producing fumes powerfully suffocating. Occurs in nature as brimstone and as a constituent of pyrites.

Tin. Sn. At. wt. 118.—A white malleable metal, stable in air. Melts at 230° C. Used largely for covering iron forming "tin plate."

Zinc. Zn. At. wt. 65.—A bluish white crystalline metal, melting at 420° C. and afterwards burning, producing a light and white powder, known as philosopher's wool. The metal is used largely for galvanising, for voltaic batteries and in the manufacture of brass and other alloys.

Molecular Weights.—The weight of a molecule on the same scale as the atomic weights is termed the "*molecular weight.*" It is dependent upon the number of atoms in the molecule and upon their individual weights. For

example, sulphuric acid contains three elements, hydrogen sulphur and oxygen. One molecule of the acid contains two atoms of hydrogen, one atom of sulphur and four atoms of oxygen. Its molecular weight is :—

2 atoms of hydrogen	$2 \times 1 = 2$
1 atom of sulphur	$1 \times 32 = 32$
4 atoms of oxygen	$4 \times 16 = 64$
Molecular weight	$= 98$

Similarly the molecule of common salt contains one atom each of sodium and chlorine, and hence the molecular weight of common salt is $(23 + 35{\cdot}5) = 58{\cdot}5$.

Chemical Formulæ.—As elements have brief designations termed symbols, so also compounds have representations which show :—

1. Of what elements they are composed, and
2. The number of atoms of each element in a molecule of the compound.

These molecular expressions are called *formulæ*. Thus, from what has just been stated, sulphuric acid is represented by the formula H_2SO_4, H_2 representing two atoms of hydrogen, S one atom of sulphur and O_4 four atoms of oxygen. The number of atoms of each element is placed as a small figure to the right-hand side of the symbol and just below it.

Again, silver nitrate has the formula $AgNO_3$, meaning first that in each molecule there is one atom each of silver and nitrogen and three atoms of oxygen.

But a further meaning is introduced into these formulæ. To each symbol is attached a quantitative as

well as a qualitative meaning. Thus Ag means, not merely silver, but an atom of silver, and as the atomic weight of silver is 108, Ag now represents 108 parts by weight of silver. Similarly N stands for 14 parts by weight of nitrogen and O_3 for 3 times sixteen parts by weight of oxygen.

Hence $AgNO_3$

$$108 + 14 + (3 \times 16) = 170$$

which is the molecular weight of silver nitrate. Not only does $AgNO_3$ stand for silver nitrate, but the expression embodies the exact composition of the substance. From the expression $AgNO_3$, the percentage composition can readily be calculated thus :—

$$\text{Silver } \frac{108}{170} \times 100 = 63{\cdot}53\%$$

$$\text{Nitrogen } \frac{14}{170} \times 100 = 8{\cdot}23\%$$

$$\text{Oxygen } \frac{48}{170} \times 100 = 28{\cdot}23\%$$

This means that with proper treatment 63·53 parts by weight of silver will produce 100 parts by weight of silver nitrate. If there is an option in the purchase of silver or the nitrate, the proportions which must be obtained are as 108 : 170.

Similarly every chemical formula is an expression of the exact chemical composition of the substance. The formula is, in fact, derived from the composition of the substance. The appreciation of these important things is more than a mere matter of academic interest.

The formula of every compound used should be studied from this point of view. A list of common compounds

used in metal coloring with their formulæ is given in Table VII of the Appendix (see p. 257).

It may next be pointed out that some compounds contain two or more simpler compounds in each molecule. Copper sulphate crystals provide an illustration. Gently heated, the blue crystals lose 36·2 per cent of water and leave 63·8 per cent of a white substance which is $CuSO_4$. These proportions are represented in the formula $CuSO_4 \cdot 5H_2O$, the 5 standing before the H_2O representing 5 molecules of water, or 10 atoms of hydrogen and 5 atoms of oxygen. True, the blue copper sulphate might be represented as $CuSO_9H_{10}$, but this is never done. $CuSO_4 \cdot 5H_2O$ more clearly expresses a loose combination of the water to the percentage mentioned :—

$$\begin{array}{c} CuSO_4 \quad \cdot 5H_2O \\ \underbrace{63{\cdot}6 + 32 + 64}_{159{\cdot}6} + \underbrace{5(2 + 16)}_{90} \\ \underbrace{\qquad\qquad\qquad\qquad}_{249{\cdot}6} \end{array}$$

$$\left.\begin{array}{l}\text{Percentage of water} \\ \text{copper sulphate crystals}\end{array}\right\} = \frac{90 \times 100}{249{\cdot}6} = 36{\cdot}2\%$$

Similarly common salt (NaCl) contains :—

$$\begin{array}{c} Na \quad Cl \\ \underbrace{23 \quad 35{\cdot}5}_{58{\cdot}5} \end{array}$$

$$\text{Sodium} = \frac{23}{58{\cdot}5} \times \frac{100}{1} = 39{\cdot}3\%$$

$$\text{Chlorine} = \frac{35{\cdot}5}{58{\cdot}5} \times \frac{100}{1} = 60{\cdot}7\%$$

while washing soda contains :—

$$\underbrace{(2 \times 23) + 12 + (3 \times 16)}_{106} + \underbrace{10 \times (2 + 16)}_{180} \quad \underbrace{\qquad\qquad}_{286}$$

$$\text{Dry sodium carbonate or soda ash} = \frac{106}{286} \times \frac{100}{1} = 37{\cdot}1\%$$

$$\text{Water} = \frac{180}{286} \times \frac{100}{1} = 62{\cdot}9\%$$

Similar calculations made on a number of common compounds frequently used will prove more than interesting. They will be helpful to an intelligent acquaintance of the materials being handled, and this will, in time, make for a fuller appreciation of the processes by which color effects are being aimed at.

CHAPTER II

CHEMISTRY—*continued*

Chemical Changes.—We now pass to a brief and general consideration of the processes which take place during the chemical coloring of metals. When chemical substances react and change their composition and properties, *chemical action* is said to occur. The atoms in the molecules undergo some rearrangement, leading to the formation of new molecules, which means new substances with distinctive properties. Chemical changes are grouped into three chief classes :—

1. Those by which two or more simple substances combine together to produce a more complex substance, or, more generally, those in which a larger number of simpler substances produce a smaller number of more complex substances. Such a change is called *synthesis* or building up. Thus copper heated in air combines with oxygen and forms two compounds—cupric oxide, CuO, which is black, and cuprous oxide, Cu_2O, which is red. Similarly the tarnishing of silver is due to the metal uniting with sulphur forming the more complex substance silver sulphide (Ag_2S).

2. Those changes by which complex substances become resolved into simpler substances. Such a process is termed *analysis*, meaning "splitting up." Thus in some coloring processes copper nitrate, $Cu(NO_3)_2$, is

heated, when it splits up into copper oxide, CuO (black), oxygen, and nitrogen peroxide, NO_2 (brown fumes).

3. In other cases chemical changes occur without apparent simplification or increased complexity of the reacting substances. In most of these changes analysis and synthesis take place together, leading to new material of no greater or lesser degree of complexity.

Chemical Equations.—We have seen that these chemical changes actually occur between the atoms and molecules of substances, and that the observable effects are the sum total of all these changes between an exceedingly large number of these exceedingly small molecules. To assist us in obtaining a clearer conception of what is actually occurring, we revert to the system of the chemists' shorthand, using symbols for the elements and formulæ for the compounds, and as these designations are used, they must convey to the mind quantitative as well as qualitative ideas. They will represent quantities of chemical substances taking part in chemical changes. Then, representing the change which occurs when magnesium burns in air, we might write it :—

Magnesium unites with oxygen forming magnesium oxide. The chemist, however, represents it thus :—

$$2Mg + O_2 = 2MgO$$

Such an expression is called a "*chemical equation.*" On the left-hand side of the equation we have the substances reacting, while on the right-hand side the substance or substances formed. But the equation means more than this. $2Mg$ represents 2×24 parts by weight of magnesium ; O_2 represents 2×16 parts by weight of

oxygen, and 2MgO represents 2 × 40 parts by weight of magnesium oxide. That, by ignition in air, 48 parts by weight of magnesium yield 80 parts by weight of magnesium oxide, is proved by a very simple test, for magnesium, thus treated, increases $66\frac{2}{3}$ per cent of its weight. The equation represents just those definite quantities of materials which by repeated tests are found to react with one another. The equation takes no account of any excesses of substances which do not react. There is, for example, bound to be a large excess of air. The excess of oxygen and the inert nitrogen find no place in the equation.

Here is another equation :—

$$Fe + CuSO_4 = FeSO_4 + Cu$$

This is a quantitative summary of what takes place when iron is put into a bluestone solution. According to the equation, iron sulphate (ferrous sulphate), $FeSO_4$, is formed and metallic copper thrown down. But the quantitative information is that 56 parts by weight of iron react with 159·6 parts of copper sulphate ($CuSO_4$) precipitating 63·6 parts by weight of copper and forming 152 parts by weight of iron sulphate. Observe that the original " water of crystallisation " in the bluestone is omitted. We make no record in these equations of any excesses of reacting materials or of substances which may be present and do not take part in the change.

If this reaction is allowed to proceed to completion the blue color will entirely disappear and the green color of ferrous sulphate will be in evidence.

Take another case. Ordinary zinc placed in dilute sulphuric acid dissolves. Bubbles of gas which, by its

lightness and inflammability, proves to be hydrogen, are evolved, and when the acid has been used up by the zinc, the clear liquid remaining yields, on evaporation, a white crystalline compound of which the formula is $ZnSO_4 \cdot 7H_2O$. The whole reaction can be done quantitatively and all weights recorded. The proportions are represented in the following equation :—

$$\begin{array}{ccccccc} Zn & + & H_2SO_4 & = & ZnSO_4 & + & H_2 \\ 65 & & \underbrace{2+32+64}_{98} & & \underbrace{65+32+64}_{161} & & 2 \end{array}$$

From the equation is omitted the water with which the acid was originally mixed, and part of which combines with the $ZnSO_4$ to form the white crystalline compound, $ZnSO_4 \cdot 7H_2O$.

It must again be pointed out that chemical equations are quantitative expressions of chemical changes which are definitely known to occur. In order to express concisely many of the changes occurring in metal coloring they will be freely used.

In our conception of chemical changes we imagine the reacting molecules broken down to either atoms or groups of atoms, and recombination occurring upon different lines. For example, hydrochloric acid (HCl) is added to a solution of silver nitrate ($AgNO_3$). A white curdy substance is thrown down in the solid form. This is evidence of its insolubility. Its composition is quantitatively expressed by the formula AgCl. The equation is :—

$$\begin{array}{ccccccc} AgNO_3 & + & HCl & = & AgCl & + & HNO_3 \\ \underbrace{108+14+48}_{170} & & \underbrace{1+35{\cdot}5}_{36{\cdot}5} & & \underbrace{108+35{\cdot}5}_{143{\cdot}5} & & \underbrace{1+14+48}_{63} \\ \multicolumn{3}{c}{\underbrace{\qquad\qquad}_{206{\cdot}5}} & & \multicolumn{3}{c}{\underbrace{\qquad\qquad}_{206{\cdot}5}} \end{array}$$

The course of the reaction appears to be :—

$$\begin{array}{ccc} AgNO_3 & & Ag \;\vdots\; NO_3 \\ \cdots\cdots\cdots\cdots\cdots\rightarrow & & \vdots \\ ClH & & Cl \;\vdots\; H \end{array}$$

Combinations such as AgClO, NH, HNO_2 or $AgClO_3$ do not here occur. It is altogether wrong to try to guess the course of a reaction and to " write up " an equation for it. The correct method is to ascertain the facts by analysis and then express them by an equation. Thus the following apparent equation is not true :—

$$AgNO_3 + HCl = AgClO + HNO_2$$

Acids, Bases and Salts.—Early in the history of chemistry some substances were known to have a sharp and sour taste and to possess the property of turning certain blue vegetable coloring matters red. These substances were called acids, and also possessed the power of dissolving and corroding many metals. Some of these substances were known as oil of vitriol, spirits of salts, aqua fortis and vinegar.

Again, other substances were known particularly for their property of turning red coloring matters blue, and when soluble in water some of them gave a distinctly soapy feeling. These substances were called alkalis, among them being caustic soda (NaOH) and caustic potash (KOH).

Now most of the well-known elements combine with oxygen and produce compounds which, as a group, are called by the chemist " oxides." Some of these oxides dissolve in water and give solutions which are like the well-known and common acids. Such oxides are said to be acidic, that is, acid-forming.

Acidic Oxides.—These oxides are produced from the non-metals and have properties closely agreeing with those of the substances commonly known as acids. More fully enumerated the following properties are common to the acids :—

1. They have a sharp and sour taste.
2. They turn blue litmus red.
3. They readily attack many metals and in some cases dissolve them.
4. When added to washing soda ($Na_2CO_3 10H_2O$) or other carbonate they evolve carbonic acid gas (CO_2) thus :—

$$\underset{\text{calcium carbonate}}{CaCO_3} + 2HCl = \underset{\text{calcium chloride}}{CaCl_2} + CO_2 + H_2O$$

5. They dissolve many metallic oxides, thus :—

$$\underset{\text{cupric oxide}}{CuO} + H_2SO_4 = \underset{\text{cupric sulphate}}{CuSO_4} + H_2O$$

$$\underset{\text{ferric oxide}}{Fe_2O_3} + 6HCl = 2\underset{\text{ferric chloride}}{FeCl_3} + 3H_2O$$

Sulphur, for example, burns to sulphur dioxide (SO_2), which, dissolved in water, produces sulphurous acid, H_2SO_3.

$$S + O_2 = SO_2$$

$$SO_2 + H_2O = H_2SO_3$$

Sulphur dioxide may be further oxidised to sulphur trioxide (SO_3), which is also soluble in water :—

$$SO_3 + H_2O = H_2SO_4$$

Basic Oxides.—The oxides of most of the metals are insoluble in water but dissolve in acids, thus destroying

the properties of the acids. Such oxides are said to be basic.

Alkalis.—A few of these metallic oxides are soluble in water. Among them are those of sodium, potassium, calcium, barium, etc. In dissolving in water these oxides definitely combine with water. The solutions formed contain new compounds with new properties. Thus sodium oxide (Na_2O) combines with water, producing sodium hydroxide (caustic soda, sodium hydrate, NaOH).

Similarly :—

$$Na_2O + H_2O = 2NaOH$$

$$K_2O + H_2O = 2KOH$$

(caustic potash)

$$CaO + H_2O = Ca(OH)_2$$

(calcium hydroxide or slaked lime)

The characteristic properties of these solutions are :—

1. They turn red litmus blue.

2. They absorb and combine with CO_2 thus :—

$$2NaOH + CO_2 = Na_2CO_3 + H_2O$$

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$

3. Some, for example NaOH and KOH, exhibit a smooth or soapy feeling.

4. They counteract or neutralise acids. Such solutions are said to be "alkaline." The dissolved compounds are "alkalis" and the oxides producing them are called alkaline oxides.

Na_2O is an alkaline oxide.

NaOH is an alkali.

Neutralisation.—On account of their totally opposite chemical properties, acids and alkalis neutralise each other. A little caustic soda solution may be colored

blue with litmus. The solution has the well-known smooth feeling. Hydrochloric acid is added a little at a time with stirring or shaking until the blue color is just permanently changed to red. This point marks the disappearance of all the alkali and the presence of the faintest trace of acid. The solution now has a pronounced saline taste, due to sodium chloride (otherwise common salt). The reaction is as follows :—

$NaOH$	+	HCl	=	$NaCl$	+	H_2O
caustic soda		hydrochloric acid		sodium chloride		water

A similar reaction occurs with sulphuric acid when :—

$$2NaOH + H_2SO_4 = \underset{\text{sodium sulphate}}{Na_2SO_4} + 2H_2O$$

Again, with nitric acid we get :—

$$NaOH + HNO_3 = \underset{\text{sodium nitrate}}{NaNO_3} + H_2O$$

These new substances, sodium chloride, sodium sulphate and sodium nitrate, may be obtained by evaporating the liquid after neutralisation. While usually white they will here be slightly colored owing to the litmus. They are neutral substances, and to these and very many similar compounds the general name of "salts" has been given. Written very generally, we get :—

ALKALI + ACID = SALT + WATER

Salts may be produced by other methods, chief among which are :—

1. Solution of basic oxides in acids.

Examples :—

(*a*) $CuO + H_2SO_4 = CuSO_4 + H_2O$
black — blue solution

(*b*) $PbO + 2HC_2H_3O_2 = Pb(C_2H_3O_2)_2 + H_2O$
litharge — acetic acid — lead acetate "sugar of lead"

or generally

Basic oxide + acid = salt + water.

2. Solution of metal in acid.

Examples :—

(*a*) $Zn + 2HCl = ZnCl_2 + H_2$
zinc chloride

(*b*) $Fe + H_2SO_4 = FeSO_4 + H_2$
ferrous sulphate

(*c*) $3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO$
copper nitrate — nitric oxide

3. Action of acid on carbonates.

(*a*) $CuCO_3 + 2HCl = CuCl_2 + H_2O + CO_2$
cupric chloride — carbon dioxide

(*b*) $PbCO_3 + 2HC_2H_3O_2 = Pb(C_2H_3O_2)_2 + H_2O + CO_2$

or generally

carbonate + acid = salt + water + carbonic acid gas.

There are other general ways by which salts may be produced, but these do not call for discussion here. It is, however, very obvious that from a wide choice of basic and acidic materials a very large number of salts will be

obtainable. Some simple system of classifying and naming them will be desirable. The accompanying table embodies such a classification, and the footnotes express general rules which are agreed practices amongst all chemists. The table is by no means complete, but every metallic compound used should be considered from this point of view and some attempt made to locate it on the general scheme.

Sulphuric Acid (oil of vitriol, H_2SO_4) is, when pure, a colorless oily liquid of specific gravity 1·84. When diluted it readily attacks many metals such as iron, zinc, magnesium and aluminium, while tin, nickel and cobalt are more slowly dissolved. The hot strong acid attacks copper, lead, mercury, silver and bismuth, evolving sulphur dioxide. With copper :—

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O$$

When mixed with water the strong acid evolves considerable heat ; in fact, the mixture may easily be raised to boiling-point. The strong acid should therefore be added slowly to the water with stirring. *Never add water to the strong acid.* When making the mixture by adding the acid to the water, thick glass vessels should not be used. The rise in temperature may cause them to crack.

It will be frequently desirable to have some idea of the strength of various samples of diluted acid. To obtain an accurate figure, chemical analysis is necessary. While to the chemist this is not a difficult matter, something simpler and more approximate is necessary in the workshop. The density of the acid is the guide. This density (weight relative to that of an equal bulk of water) is readily found by means of one of the common forms of

Salts prepared from	Are called	And with the metal contain	For example:—
Sulphuric acid	Sulphates	SO_4	Lead sulphate ($PbSO_4$); silver sulphate (Ag_2SO_4).
Hydrochloric acid	Chlorides	Cl	Silver chloride ($AgCl$); gold chloride ($AuCl_3$); platinum chloride ($PtCl_4$).
Nitric acid	Nitrates	NO_3	Silver nitrate ($AgNO_3$); lead nitrate $Pb(NO_3)_2$.
Hydrocyanic acid	Cyanides	CN	Potassium cyanide (KCN); silver cyanide (AgCN).
Acetic acid ($HC_2H_3O_2$)	Acetates	$C_2H_3O_2$	Copper acetate ($Cu(C_2H_3O_2)_2$); lead acetate ($Pb(C_2H_3O_2)_2$).
Phosphoric acid (H_3PO_4)	Phosphates	PO_4	Calcium phosphate ($Ca_3(PO_4)_2$); sodium phosphate (Na_3PO_4).
Oxalic acid ($H_2C_2O_4$)	Oxalates	C_2O_4	Potassium oxalate ($K_2C_2O_4$).
Tartaric acid ($H_2C_4H_4O_6$)	Tartrates	$C_4H_4O_6$	Potassium bitartrate (cream of tartar) ($KH{\cdot}C_4H_4O_6$).
Carbonic acid (?)	Carbonates	CO_3	Sodium carbonate (Na_2CO_3); calcium carbonate ($CaCO_3$).
Sulphurous acid (H_2SO_3)	Sulphites	SO_3	Sodium sulphite Na_2SO_3; potassium bisulphite ($KHSO_3$).
Hydrosulphuric acid (H_2S)	Sulphides	S	Silver sulphide (Ag_2S); copper sulphide (Cu_2S); barium sulphide (BaS).
Nitrous acid (HNO_2)	Nitrites	NO_2	Sodium nitrite ($NaNO_2$).

From this table it will be noticed that most of the acids contain oxygen, and the name of their salts terminates with *ate* or *ite* according to the quantity of oxygen present. Thus :—

(1) When the larger quantity of oxygen is present the termination is *ate*, e.g. sulphate, nitrate, etc.

(2) When the smaller quantity of oxygen is present the termination is *ite*, e.g. sulphite, nitrite, etc.

hydrometer. In the Twaddell instrument the reading (n) which coincides with the level of the liquid is converted to density in the following manner :—

$$\text{Density} = \frac{(n \times 5) + 1000}{1000}$$

With the Beaume instrument density is found from the scale reading (x) as follows :—

$$\text{Density} = \frac{144}{144 - \text{degrees Beaume}}$$

A Beaume hydrometer is also constructed for liquids lighter than water. With it :—

$$\text{Sp. Gr.} = \frac{144}{134 + \text{degrees Beaume}}$$

The density thus found is compared with Table No. II in the Appendix. Thus a dilute sulphuric acid recorded 40 on the Twaddell scale. Its density is therefore 1·2, and 27 per cent of the acid by weight is H_2SO_4. Similar methods can be used for other acids and very many solutions.

The sulphates, with the exception of those of barium, lead and strontium, are soluble in water. They, as well as the free acid, may be detected by the addition of HCl and barium chloride solution, when a heavy white and insoluble precipitate of barium sulphate occurs :—

$$H_2SO_4 + BaCl_2 = BaSO_4 + 2HCl$$
$$CuSO_4 + BaCl_2 = BaSO_4 + CuCl_2$$

Hydrochloric Acid (muriatic acid, spirits of salts, HCl) is made commercially by heating rock salt (NaCl) with oil of vitriol, when :—

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$$

At ordinary temperatures the acid is a fuming gas, very soluble in water. The manufactured gas is absorbed in water in suitable towers, and the solution constitutes the acid of commerce. The strongest acid has a density of 1·2 and contains 41 per cent of HCl. For many purposes it is further diluted. (See Table III of densities and composition in Appendix.) When pure the acid solution is colorless, but the common acid is invariably yellow, due to impurities. The acid readily attacks magnesium, aluminium, cadmium, iron, manganese, nickel, tin and zinc, while arsenic, lead and bismuth are but slowly attacked. With silver, a very slight film of silver chloride is formed on the surface of the metal and, being insoluble, protects the metal from further attack of the salts. Mercurous chloride is also insoluble, while that of lead is only slightly soluble in cold water, but dissolves freely on boiling.

The presence of the acid or a soluble chloride is readily detected by the addition of nitric acid and a solution of silver nitrate, a white curdy precipitate (AgCl) being formed :—

$$NaCl + AgNO_3 = AgCl + NaNO_3$$

This precipitate is soluble in ammonia and reprecipitated by HNO_3.

Nitric Acid (aqua fortis, HNO_3) is obtained by the action of oil of vitriol on Chili nitrate (natural sodium nitrate).

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$$

As first produced it is a yellowish liquid (aqua fortis), but the purest and strongest acid has a sp. gr. of 1·53 ; it rapidly stains the skin and other organic matter yellow. When strong it rapidly attacks and dissolves copper, lead,

nickel, mercury, silver, bismuth and zinc, but antimony and tin are converted into insoluble oxides. It thus constitutes an excellent cleaning liquid for copper and most of its alloys such, for example, as the brasses.

The acid does not attack either gold or platinum, but the addition of hydrochloric acid gives a mixed acid known as aqua regia, which, liberating chlorine, effects the solution of the two metals thus :—

$$3HCl + HNO_3 = Cl_2 + NOCl + 2H_2O$$
$$Pt + 4Cl = PtCl_4$$

The salts of nitric acid are called nitrates. Practically all the nitrates are soluble in water.

Acetic Acid ($HC_2H_3O_2$) is obtained by distilling calcium acetate with acid :—

$$Ca(C_2H_3O_2)_2 + H_2SO_4 = CaSO_4 + 2HC_2H_3O_2$$

This acid can be concentrated up to nearly 100 per cent. When strong it freezes at ordinary temperature and is then called glacial acetic acid. Vinegar is an impure and dilute form of the acid obtained by the fermentative oxidation of alcoholic liquids. Its salts are called acetates, and those of copper and lead are much used in metal coloring. Copper acetate is $Cu(C_2H_3O_2)_2$ and lead acetate $Pb(C_2H_3O_2)_2$. A modification of copper acetate is called verdigris. Lead acetate is used for the deposition of lead, for the production of metallochromes and for the coloring of brass.

Potassium Hydroxide (potassium hydrate, caustic potash, KOH) occurs in commerce in the form of cakes or sticks. It dissolves freely in water or alcohol. Its main purpose in cleaning metal work is for removing grease. This is converted into soluble materials which then

dissolve in the water of the solution. As an example of the greasy or fatty materials removed by potash, stearine may be taken. Then :—

$$\underset{\text{stearine}}{C_3H_5(C_{17}H_{35}COO)_3} + \underset{\text{potash}}{3KOH} = \underset{\text{glycerine}}{C_3H_5(OH)_3} + \underset{\substack{\text{potassium}\\\text{stearate}\\\text{(soft soap)}}}{3C_{17}H_{35}COOK}$$

For such cleaning purposes an impure but cheap variety suffices.

Ammonium Hydroxide (ammonium hydrate, ammonia, spirits of hartshorn, NH_4OH) is a solution of ammonia gas (NH_3) in water. The strongest solution of commerce has a sp. gr. of ·880 (hence the term 880 ammonia). It contains about 36 per cent NH_3. More dilute solutions have higher sp. grs. (see Table V in Appendix). It must, of course, be kept in well-stoppered bottles. It neutralises acids forming the ammonium salts, e.g. the chloride (sal-ammoniac) NH_4Cl and sulphate $(NH_4)_2SO_4$. NH_4 does not exist as a separate substance. Ammonium compounds and the solution of the gas find frequent application in electro-plating and metal coloring.

CHAPTER III

ACTION OF AIR ON METALS

Corrosion of Metals.—The fact that few metals are naturally incapable of withstanding for long the exposure to atmospheric and other corrosive conditions ordinarily attaching to everyday service, is too well known to need recall. Few people, however, have any idea of what rusting and corrosion mean in general industry. A piece of bright iron rusts quickly on exposure to damp air, and scientists are not yet exactly agreed as to what are the real underlying causes. Much investigation during the past two decades has, however, considerably enlarged our knowledge of the whole problem.

Sir Robert Hadfield, the inventor of manganese steel, has estimated that the rusting of iron is costing the world in maintenance and depreciation charges no less than £500,000,000 per annum. Such are the "ravages of rust," the "rat that eats steel." As rusting is strictly a case of chemical combustion, rusting can be aptly described as an eternal and flameless fire. We obtain all our iron and steel from natural materials which are of the nature of rust, and when, by much labour, the iron is extracted from the ore and put into service, it promptly starts, unless definitely prohibited, degenerating back to rust.

Certain special cases of iron alloys are practically stainless and rustless. These are relatively costly materials,

and we are far from what one may call a rustless iron age. At present we have to fight the enemy rust. This is done by mechanical methods or by the application of chemically durable coatings. Such coatings consist of metals, of which zinc and tin are notable examples, or of non-metallic materials, such as paints and varnishes. A consideration of each of these is a large subject, outside our immediate object.

A further alternative, however, suggests itself. If the product of rusting is a stable product, why not coat the iron with a uniform and adherent layer of such substance and so prevent any further change ? Such a method has, with considerable advantage, been followed.

But iron does not stand altogether alone in its corrodibility. Very few of the ordinary metals escape such a disintegrating influence. Gold and platinum are the only two ordinary (well-known) metals which are resistant to the corroding conditions of everyday service. Copper, zinc, aluminium, lead, tin, nickel and silver all suffer, and, for permanence, need some protection. Many of the metals, too, have colors which cannot be regarded as anything but monotonously dull, and some variation in the color scheme of the metals would certainly be welcome. These decorative and non-corrosive ends can very frequently be simultaneously achieved by a simple and single process. With such processes this book is concerned.

Rate of Corrosion.—Now the rate of corrosion varies very much with different metals, and even with the same metal under different conditions. Readers with the facilities would be well advised to try the effects of the following liquids on clean iron nails standing only partly

ıbmerged in them. Such instructive liquids are: rdinary water—usually "tap" water—distilled water, ell-boiled distilled water cooled out of contact of air, ater containing a trace of acid, water containing a little lkali (e.g. NaOH) and water containing hydrogen eroxide (H_2O_2). A good deal of suggestive information ıight be forthcoming from such experiments.

In the atmosphere there are many constituents which ıight contribute to the staining, corrosion and rusting f metals. There are, for example, oxygen, moisture, arbonic acid gas and quite a number of acids. Sulphuric cid in the atmosphere results from the combustion of oals containing sulphur. Most coals contain *at least* per cent of sulphur. One half of this sulphur may emain in the ashes from the coal and the other $\frac{1}{2}$ per cent asses off as sulphur dioxide (SO_2), which is quickly onverted to sulphuric acid. A consideration of the ollowing expressions:—

$$S + O_2 \longrightarrow SO_2\,;\quad SO_2 + O + H_2O \longrightarrow H_2SO_4$$

mpresses the fact that 32 parts by weight of sulphur ield 98 parts by weight of pure sulphuric acid, and a imple calculation shows that 100 tons of coal during ombustion contributes $\frac{1}{2} \times \frac{98}{32} = 1\frac{1}{2}$ tons of sulphuric cid to the atmosphere. No wonder the atmosphere is orrosive! Again, nitric acid in the atmosphere is a roduct of an electric discharge such, for example, as in hunderstorms.

Order of Corrodibility of Metals.—Now chemists ıave made a comprehensive and careful study of the ffects of all these corrosive conditions on each of the netals, and, in a general way, they have been able to ırrange the common metals in an order in which they

appear to be susceptible to corrosive conditions. The order is as follows: magnesium, aluminium, zinc, cadmium, iron, nickel, tin, lead, copper, silver, mercury, gold and platinum. The list in parts may occasion some surprise, being apparently contradictory to experience. For example, zinc might be regarded in everyday life as more enduring than iron, for zinc is used in galvanising as a protective coating for iron. So it is, and for two reasons :—

1. When zinc is oxidised it forms a thin film of adherent oxide. This adherent oxide protects the metal. The same may also be said of aluminium, tin, lead and copper. On the other hand, when iron rusts the product is bulky, loose, non-adherent, and actually attracts moisture and in many ways encourages further action. For that reason rust should be entirely eliminated before any attempt is made to apply protective coatings to iron and steel.

2. When galvanised iron is, in the course of erection or use, damaged to the extent of puncturing the zinc coating and exposing the iron, the two metals, side by side, electrochemically co-operate to protect the iron at the expense of the zinc.

The zinc is thus correctly placed in the list with regard to iron. Much therefore depends also upon the nature of the products of corrosion.

The general permanence of such metals as aluminium and zinc under atmospheric conditions, in which appreciable quantities of acids are not present, justifies some hope that films of oxides might be produced artificially and render good service as inhibitors of corrosion. That hope is realised in practice.

Sulphuretted Hydrogen (H_2S) constitutes another

staining influence in the atmosphere, especially where coal and coal gas are being consumed. This gas attacks the white lead (say, lead carbonate, $PbCO_3$) in lead paints, and converts it to dark brown or black lead sulphide (PbS).

$$PbCO_3 + H_2S = PbS + H_2O + CO_2$$

Zinc white paints are not susceptible to this discoloration, because zinc sulphide is still white. But H_2S also attacks some of the metals. It rapidly tarnishes copper and silver, producing films of their sulphides, Cu_2S and Ag_2S. The discoloration of polished copper and silver, especially in foggy weather, is a sufficient illustration of this. Once again the evil may suggest means of its removal, and the production of films of sulphides by means of sulphuretted hydrogen and its allied compounds is largely resorted to.

Carbonic Acid Gas is definitely known to make substantial contributions to the rusting of metals. In the case of iron the following cycle of operations is generally agreed upon :—

Carbonic acid gas and moisture form a very weak acid, carbonic acid (H_2CO_3). This attacks the iron :—

$$Fe + H_2CO_3 = FeCO_3 + H_2$$

Ferrous carbonate ($FeCO_3$) is a known, though not a large, constituent of rust. It is, however, unstable, and undergoes further changes, thus :—

$$2FeCO_3 + O + 3H_2O = Fe_2O_3{\cdot}3H_2O + 2CO_2$$

Hydrated ferric oxide ($Fe_2O_3{\cdot}3H_2O$) may be taken as approximately representing iron rust. It will be seen that the CO_2 is liberated and is free to attack more iron and carry on its insidious work. Experience confirms this. It is useless to paint over rusty iron. Specks of rust under

the paint promote further rusting, which blisters off the coating of paint and exposes large patches of metal.

Carbonic acid gas also plays an important part in the production of those beautiful green antique effects common to bronze statuary. Here the acids in the air first attack the bronze, and the copper compounds produced are converted to green basic carbonates which are insoluble in water and therefore of a permanent character.

Corrosion and Rusting.—While, as has been said, we now know so much about the general effects of the atmosphere on the metals in everyday use, it has still to be admitted that our present knowledge is altogether inadequate as compared with the tremendous costs entailed by such corrosion. In fact, it has recently been suggested that future generations will marvel at our ignorance of the whole problem in an age of admittedly great scientific advances. Be that as it may, it will nevertheless have to be admitted that we are alive to the importance of the problems and energetic in solving them, even if late.

The problems are by no means simple. The conditions are so extremely variable, and probably no two experimenters work under exactly comparable conditions. Attempts have nevertheless been made to follow the processes scientifically, and, moreover, to attach to the terms in common use some definite meaning. Tarnishing, rusting, corroding are terms somewhat vaguely used. Some clearer definition is desirable.

Take the case of iron. The deterioration is recognised as a two-step process :—

1. The metal is to a very slight extent dissolved by

acid which can probably never be entirely absent under everyday conditions. This solution or dissolving process is called *corrosion*. A metal may easily be attacked by acid and yet remain clean. This occurs, for example, in the ordinary pickling and dipping processes in which the dissolved metal is washed away either by the acid or by means of rinsing water.

2. Many of these compounds, however, are in everyday use not washed away. They cling to the surface of the metal and are subsequently decomposed, depositing insoluble compounds of the metal and liberating some constituent which is then free to recarry on the whole process cyclically. This precipitation stage may be called *rusting*, and the term is thus given a wider application than its previous limited use in the case of iron and steel.

The Tarnishing of Metals in Air.—These two processes, while chemically quite distinct from each other, nevertheless take place simultaneously, and the initial appearance of the final product is what is called *tarnishing*. This refers to the merest films of products, and not the wholesale wearing away of the metal. It is no less important, however, in that it very considerably determines the course of subsequent changes.

A very thorough research has recently been carried out by Mr. W. H. J. Vernon, B.Sc., for the British Non-Ferrous Metals Research Association, with the object of studying the relative behaviour of different metals when exposed to atmospheric influences, both indoors and outside. The results were embodied in a paper* before the Faraday Society, which will well repay close study

* "Trans. Faraday Society," 1924.

both on account of the methods used and the results obtained.

This investigation brought out for the first time the marked difference in the mechanism of corrosion with different metals, and this discovery will doubtless prove very helpful from both the practical point of view in the selection of metals for domestic and constructional purposes, and also in the elucidation of the whole question of corrosion.

Three different types of tarnishing have been distinguished :—

1. In the first type, represented by copper, the tarnish film actually protects the metal from further attack, the progress of tarnishing becoming slower and slower as exposure was continued. This was accounted for by the supposed continuous layer which the tarnish film forms, and the consequent difficulty the corroding constituents of the air find in reaching the underlying metal.

2. In the second type, the tarnish is neutral and the attack proceeds steadily. This appears to be the case with zinc in a dry atmosphere. The film of tarnish is probably pervious.

3. In the third type, corrosion may start off slowly, but later on accelerate. This is evidently the case with iron, where the rust formed—as has been shown above—assists in the attack.

Having recognised these three types of tarnishing, it does not necessarily follow that a single metal follows only one of them. Some metals, such as zinc and brass, follow more than one. Brass, for example, is first attacked uniformily for a time, but later the film exhibits a protective influence and the attack slows off.

Nickel, again, offers a somewhat different problem. It is, as is well known, very permanent in air, but seems to condense on its surface a fog or cloudiness which can be readily removed by washing with alcohol, thus restoring the bright metallic surface underneath.

It may, incidentally, be mentioned that one of the methods used in following the tarnishing process was the loss of reflecting power of the original surface which was perfectly flat and bright.

Summary.—It may be of advantage to conclude this chapter by a tabulated statement of the behaviour of the common metals in air at both ordinary and high temperatures. In such a table the information must necessarily be but briefly expressed, and conciseness may carry a lack of preciseness. Taken somewhat generally, however, the data is in a compact form, and should be useful for reference until a fuller knowledge has been gained by the experience of handling the metals.

BEHAVIOUR OF METALS WITH AIR

Metal.	Color.	Effect at Ordinary Temperature.	Effect at High Temperature.
Aluminium	White	Remains bright.	At red heat burns with white light, giving Al_2O_3.
Antimony	White	Remains bright.	Oxidises at M.P., producing Sb_2O_3 (white).
Arsenic	Greyish white	Gradually tarnishes.	Readily oxidises to As_2O_3 (white).
Bismuth	Reddish white	Unaltered in dry, but tarnishes in moist air.	When strongly heated burns to Bi_2O_3 (yellow).
Cadmium	White	Remains bright in air free from CO_2.	Burns to CdO (brown).
Chromium	Steel grey	Remains bright.	Superficial oxidation to Cr_2O_3.
Cobalt	Grey-white	Unacted on by dry air. Slowly oxidised by moist air.	Burns with red light when strongly heated.
Copper	Red	Unacted on by dry air. CO_2 and water cause tarnishing, as also does H_2S.	Forms Cu_2O and CuO at low temperature. Burns at high temperature.
Gold	Yellow	Does not oxidise.	Does not oxidise.
Iron	White-grey	Dry air, no action. Rusts in moist air.	Oxidises to Fe_3O_4 (black).
Lead	Bluish white	Tarnishes.	First forms PbO (yellow), then Pb_3O_4 (red lead).
Manganese	Steel grey	Oxidises to Mn_3O_4.	Oxidises to Mn_3O_4.
Mercury	White	No action.	At nearly its B.P. forms HgO (red).
Nickel	White	Little action.	Forms NiO.
Platinum	White	No action.	Unaffected.
Potassium	Slightly violet	Rapidly tarnishes.	Burns violet flame, forming K_2O_4 and K_2O.
Silver	White	Unaffected. Turns black if H_2S is present.	Not oxidised, but melted metal occludes oxygen.

CHAPTER IV

GENERAL METHODS OF COLORING

Introduction.—It may with safety be said that the multifarious methods of chemical metal-coloring do not lend themselves to easy classification, and any attempt at systemising them may be handicapped by overlapping and indefiniteness. Yet, as scientific principles are involved, some simple grouping is possible.

The aim of the colorer is the production of color effects on the surfaces of metals chiefly, and occasionally other materials. These color effects may be obtained by producing colored films, or indeed by means of films devoid of color themselves, yet producing colored effects.

General Methods of Metal-Coloring.—Speaking generally, there are four different ways of doing this. There are:—

1. *Mechanical methods,* in which a definitely colored material is applied to the surface of the metal by some system of dipping, painting or spraying.

2. *Thermal methods,* in which the application of heat effects the formation of colored or color-producing films. Such films are usually oxides.

3. *Chemical methods,* in which the films are produced by the interaction of the metal with some chemical substance. This is a very commonly applied method, and

4. *Electrolytic methods,* in which films of metals, oxides,

or even other compounds are obtained by electrolytic action, metal films being deposited at the cathode and oxide films at the anode.

Simple examples of each may be cited.

In *Mechanical methods* it is assumed that the color effect is due to the film which is definitely added to the surface of the metal, and in which the metal surface undergoes no change of composition. Several of these methods are referred to in Chapter XIX under various processes. The application of colored lacquers would come under this heading.

Thermal methods are illustrated in the colors produced on steel with the rise in temperature which accompanies tempering. Indeed, most metals with colored oxides can be somewhat similarly treated, a good case being that of copper, which at a moderate temperature produces red to brown cuprous oxide (Cu_2O), while at a higher temperature black cupric oxide (CuO) results.

Chemical methods assume some definite chemical change to the surface of the metal. Thus copper and brass in solutions of copper nitrate or sulphate are oxidised, and these solutions, especially when made alkaline with ammonia, also deposit the oxides on heating. Similarly, the surface of copper is definitely converted to sulphide when this metal is brought into contact with any soluble sulphide. Thus

$$2Cu + K_2S + H_2O = Cu_2S + 2KOH + H_2$$

In the same category also must be placed those reactions which, without the application of externally produced electrical effects, lead to the formation of metallic films by what is called simple immersion. The production of films of arsenic and antimony on copper and brass goods

provides a good illustration, as does also the deposition of platinum on silver by the platinising process.

Electrolytic methods cover the production of films of colored metals of which there are numerous examples, and also the production of oxide films at the anode, this being exemplified in the anodic deposits of lead peroxide (PbO_2), giving rise to "Nobili's rings."

These methods will be in general controlled by conditions such as usually operate in the processes of electroplating. They will be best realised by the simultaneous attainment of conditions both chemical and electrical. Exactitude in the production of these conditions best ensures success. As the electroplater is well aware, there are numerous variable factors which influence the character of a metal deposit. These need not now be enumerated, but when it is remembered that they may operate singly or together, it will be realised that any such operation cannot be expected to be successful unless there is prior knowledge of the best conditions, and some very definite attempt to attain them. In the usual course of experimental work on electroplating these very definite conditions are realisable and realised. The everyday jobs of the trade, however, make it difficult to exactly apply the lessons of such research. Each worker must, with the general knowledge attainable, assume the rôle of a researcher and find the best conditions for his own class of work, and having made a record of them, use them as a guide for the future. Such instructions as are given can only be taken as an approximate guide.

Large and Small Scale of Working.—A little experience soon shows the difficulty in the exact reproduction of conditions essential to definitely desired shades of color.

This becomes very obvious with a change in the scale of operations. Assume for a moment that a definite temperature is essential, as it often is. The maintenance of a definite temperature is an easier proposition on a larger than on a smaller scale from every point of view, so many circumstances arising which may cause some alteration of temperature. Or assume that a definite composition of liquid is required at a high temperature. Unavoidable evaporation will make a bigger change of composition to a small bulk of liquid contained on a shallow vessel, than to a larger bulk contained in a deeper vessel. Again, definite electrical conditions may be required for the production of some of the black nickels referred to in Chapter XVI, or the metallochromes in Chapter XVII. In the former case low-current densities are the usual order. Under usual workshop conditions these are not easily and repeatedly obtained with any exactitude. Early experiments with mere drops of solutions will create difficulties which will disappear on a larger scale. But this larger scale work will not diminish the need for accurate control and observation. Frequently there is a latitude in the conditions which, while it may aid the beginner, must not be relied on as a substitute for careful work and accurate observation. Intelligence rather than ignorance will make the best use of such tolerances of conditions of working.

Chemical Operations.—It may be recalled that most of the common metals occur in nature as chemical compounds, amongst the chief of which are the oxides, sulphides and carbonates. Some of these compounds have naturally quite a beautiful aspect. The metallurgist decomposes these raw materials and extracts the meta

herefrom. Once set free, the metals have a natural endency to revert to their more original forms. These eversions proceed slowly under daily conditions of xposure. The metal colorer carries forward such perations much more rapidly, and obtains pleasing esults by the exercise of control over a number of conditions which co-operate to that end. His object is to chieve a result rapidly without sacrificing any element f beauty. Rapidity of operation is gained by the use of ctive chemical substances aided often by heat, for hemical actions do most frequently accelerate with an levation of temperature.

Many of these chemical changes, while they produce pparently simple results, are not in themselves so very imple. The exact course of the action, while a matter of reat interest, is to the practical colorer of less importance than the reproducible conditions controlling hem. A good deal of work might be done on the hemistry of many of these operations. Only occasionally ave such chemical experiments been made. Such work hould appeal most to the student of chemistry with a nowledge and interest in metal coloring operations, nd would provide a useful and attractive field of esearch.

Chemical Activity of Metals.—Where chemical change s concerned it will be recognised that all metals vary in ctivity. Some metals dissolve rapidly in acids, others nore slowly. No other metal appears to corrode with uite the same speed as iron. Metals like platinum and old may be judged from their permanence in the air to e comparatively inactive. This variation in activity vill certainly have some influence in metal-coloring

processes. A knowledge of the comparative activities o the metals is of considerable use.

Such a comparison, however, is not to be made by an casual observation. For example, it would appear fron the rapid rusting of iron and the comparative stability o zinc on galvanised iron, that iron is the much more activ metal. This conclusion would be wrong. A wide knowledge of the chemical behaviour of the metals i necessary, and from this wider point of view zinc i universally recognised as a much more active meta than iron.

Chemical actions are frequently accompanied by th evolution of heat. Energetic reactions evolve much heat Slow reactions give little heat. Chemical actions wit zinc as a very general rule evolve more heat than thos with iron. This is so when both metals are comparabl converted into their oxides, sulphides or chlorides.

Again, the compounds formed vary in stability. Zin compounds are more stable than those of iron. Zinc i more difficult to recover from its compounds and fron its ores than is iron. The activity of such metals a aluminium, magnesium, sodium and zinc is illustrate by the fact that these metals never occur free in nature while the occurrence of free gold, silver, mercury an platinum is a testimony to their comparative chemica inactivity.

Electro-chemical Series.—A study of the chemistry o the more common metals places them in the followin order as regards chemical activity: Sodium, magnesium aluminium, zinc, iron, nickel, tin, lead, copper, arseni antimony, mercury, silver, platinum and gold. The firs mentioned metals are obviously the more active. The orde

; not inflexible ; under some conditions the order may be eversed. Iron is more active than tin under conditions of cidity, but the reverse holds under alkaline conditions. The list may be said to embody the average behaviour f the metals. From it, general conclusions may be rawn. Up till quite recently the more active metals ave been described as electropositive metals, and the ess active metals electronegative. There are, however, ound scientific reasons for reversing these terms, and his course has been decided upon by the scientific bodies. Until the newer system is more generally adopted, and as n the period of transition confusion is apt to arise in omparing notes in which both systems have been used, ve shall avoid any such confusion by refraining from sing the terms, but using rather the unmistakable erms, more active and less active. The term inactive, oo, would not be wise. Some elements are inactive ; hey do not enter into any chemical combination. We re not now concerned with such elements, hence the omparative terms more active and less active are dequate. This order given above is commonly known s the electro-chemical series.

Illustrations of the Principle.—Illustrative of the nformation embodied in this series, a few fairly well-nown facts may be recalled. Sodium oxidises so rapidly n air that it is ordinarily preserved under mineral oil. t even burns when placed on water. The seeming ermanence of aluminium and zinc in an ordinary tmosphere where the " less active " iron rapidly rusts is ue entirely to the protective character of a very thin lm of tenaciously adherent oxide, which repels rather nan attracts moisture. The rust produced on iron is

bulky, loose and disintegrates. It attracts moisture and progressively encourages further rusting.

Again, zinc is used for covering iron and steel as a means of protection. It acts in a twofold manner. As long as the coating is continuous it functions as zinc, but when the surface of zinc is worn or scratched through, the zinc still acts protectively in being eaten away around the bared iron in preference to the iron. On the other hand, the tin coating on tinned iron is effective only so long as the coating is perfect. As soon as any iron becomes exposed the tin promotes rusting of the exposed iron. This is very obvious in common tinware after some use.

Simple Immersion.—Again, where the chemical changes result in the deposition of colored films of metal, the same well-known law and order rules. Quite obviously each metal cannot replace every other metal. Zinc replaces copper and copper replaces silver, but these reactions are not ordinarily reversible.

By careful observation the order in which metals replace one another has been found to be that in which they enter into active chemical action, as shown in the preceding section. Table I puts this information in another form, from which a good idea can easily be gathered as to the prospects of successful deposition of metals by simple immersion.

Such films of metal can only be thin, for as soon as the original metal is covered with the deposited metal, further action must necessarily cease.

Yet another point is noticeable. If deposition by simple immersion takes place rapidly, as for example with zinc in copper sulphate, the deposited metal is very loose,

ark and powdery, and the process is only available as means of extracting from a solution a more costly metal y means of a cheaper but more active metal. If deosition by simple immersion takes place slowly, there ıay be a good chance of obtaining a thin, bright and

TABLE I

Solution.	Metal.												
	Zn	Pb	Cu	Cu Zn	Cu Zn Ni	Fe	Ni	Sn	Sb	Ag	Hg	Pt	Au
Zic sulphate .	n	n	n	n	n	n	n	n	n	n	n	n	n
Lad acetate .	d	n	n	n	n	n	n	n	n	n	n	n	n
Stnnous chloride	d	d	n	n	n	n	n	n	n	n	n	n	n
ACN·KCN .	d	n	d	d	d	n	n	n	n	n	n	n	n
Copper sulphate	d	n	n	n	n	d	n	d	n	n	n	n	n
ACN·KCN .	d	d	d	d	d	n	n	n	n	n	n	n	n
Mrcuric nitrate	d	d	d	d	d	d	d	d	d	n	n	n	n
Sver nitrate .	d	d	d	d	d	d	d	d	d	n	n	n	n
Platinum chloride	d	d	d	d	d	d	d	d	d	d	d	n	n
Gld chloride .	d	d	d	d	d	d	d	d	d	d	d	d	n

d = deposition. n = non-deposition.

dherent film of the deposited metal. Where simple nmersion is applied in metal coloring this is the aim, ıd these conditions lead to the achievement of the esired result.

Colors of Compounds.—Now many oxides, sulphides ıd carbonates have well-defined colors, but these vary

very much according to the method of preparation. When such a compound as mercuric iodide may be yellow or red, we can only deduce that color is not so very definite a property. Metals have fairly distinctive colors, but as fine powders many of them may be very dark and nearly black. Shades vary with the state of aggregation. Powdered salts are frequently much lighter than the bigger crystals. This can be observed in the case of copper sulphate, and is due to a large amount of reflection of white light between the multitudinous small crystals.

It is quite a common observation that natural compounds have quite a different color from those prepared in the laboratory. Mercuric sulphide (HgS) occurs naturally as cinnabar. This is a red mineral. By precipitation the color varies from white through red to black. Lead sulphide (PbS) occurs as galena. This is a bluish-grey mineral, yet by precipitation the same compound is black. The iron sulphides are yellow in nature, but ferrous sulphide is black by preparation. Such variations in color would seem to widen the opportunities for producing color effects on metals by chemical action.

Again, we usually view gold by the light which is reflected from it. It then exhibits the well-known yellow color. Seen through a thin film, as in the case of gold leaf, the metal appears green. Thus as to whether the light which comes from an apparently colored substance is reflected or transmitted may influence the color. It may thus even be that a film of colored compound may be so thin that light actually penetrates it and is reflected back from a polished surface of metal below. This very

frequently occurs. So thin may the films be, that the natural color of the compound is quite overshadowed by the effects of the light transmitted by this reflection from the polished basis metal. A good illustration of this is seen in the varying colors produced by thin films of lead sulphide on brass (see p. 160), while another case is that of the orderly change of color occurring, due to the formation of an increasingly thicker film of oxide of iron on steel which is being tempered.

Thickness of Films.—It will be readily recognised that the films of oxides and other deposits produced in metal-coloring processes must be exceedingly thin. Experiments have from time to time been made to determine the weight of such deposits. To this end Mr. T. J. Baker, of Birmingham, made many interesting experiments. The color films were dissolved off by means of potassium cyanide solution or dilute sulphuric acid, which did not attack the basis metal and the loss in weight determined. In one case a black film (CuO), produced by dipping in a solution of copper nitrate and heating, gave a weight of 99 milligrams per square decimetre. This represents 14 grains per square foot. Black films (CuO), obtained by immersion in ammoniacal copper carbonate solution, gave 37 milligrams per square decimeter (5·3 grains per square foot). Films of Cu_2O obtained on copper from copper nitrate solution weighed 50 milligrams per square decimeter (7 grains per square foot), while the brown film produced on brass in hot copper chloride solution weighed 21·5 milligrams per square decimeter (3 grains per square foot), with a loss of metal of 77 milligrams per square decimeter (11 grains per square foot). An average of eight determinations gave 62

milligrams of color film per square decimeter (or about 9 grains per square foot). These results cannot pretend to uniform accuracy. The processes and conditions are too variable. What they do show is the generally small amount of color material which effectively produces the desired effect.

Putting the figure in another form and assuming that a color material has a density of 2, a film of 9 grains per square foot represents a thickness of one-eight-thousandth of an inch.

Some Color Effects.—Now sunlight is not a simple kind of light. It is composite, and its components are sorted out and ranged side by side in many ways. The rainbow is one such effect produced by the analysis of sunlight as it passes through a mist of fine water-drops. A similar sorting out takes place when white light passes through almost any irregularly shaped piece of glass, for example, a bevelled edge. This effect is much more accurately and strikingly produced when light passes through a wedge-shaped prism of glass, or a similarly shaped bottle containing a liquid like carbon disulphide. The colored band of light thus produced is called the spectrum, and on it can readily be distinguished successive bands of red, orange, yellow, green, blue and violet. These bands merge one into the other, and several of these colors are still complex and can be split down into simpler colors.

There appear to be three primary colors which are incapable of being further split up and which, compounded together, yield every known color shade. These are red, a rather yellowish green and a blue-violet. Reverting, however, to the obvious colors of the spectrum, each of the constituents, red, orange, yellow, green, blue and

violet, have different properties. They may be regarded as different kinds of light. Put together in the correct proportion they reproduce white light.

Now all substances which are said to be colored, effect some analysis of light. A yellow substance absorbs all kinds of light except the yellow, and this it reflects. Similarly a blue substance absorbs all colors and reflects only blue. Viewed in red or yellow light a blue substance looks black.

With thin films, quite new effects are to be observed. Such thin films are those of soap bubbles with their beautiful colored effects and the thin films of oil which form on water. We see many examples of such films of oil on wet roads, and some charming effects are then obtained.

When light passes through such films it suffers some decomposition or sorting out, and the thickness of the film plays an important part. With very thin films, increasing thickness brings color effects in a definite order, such for example as those already referred to on page 49. With a circular film which decreases in thickness from the centre to the circumference, these colors succeed one another in a regular series of colored rings. These are illustrated in Nobili's rings (see page 222). As the film becomes sensibly thick it becomes opaque and dark brown. This type of ring was first obtained by Sir Isaac Newton by gently pressing a slightly curved piece of glass on to a flat glass surface. Between the two glasses there was a thin film of air increasing in thickness from the centre of contact. The rings produced were then known as Newton's rings. Metallochromes reproduce this effect with a regularly varying film of lead peroxide produced on a polished iron or nickel anode in a lead solution.

CHAPTER V

MECHANICAL CLEANING OF METALS

Necessity for Cleanliness.—One of the most important requirements for work to be electroplated or bronzed is that of cleanliness. For this purpose ordinary household cleaning is, in itself, quite useless. Nothing short of chemical cleanliness will suffice. Dirt was once defined as "matter out of place," and thus practically all work which comes from the factory is extremely dirty, carrying, as it does, sand in the case of castings, oxide scale on almost all work and grease on every sample of metal which has, in any way, been worked or even handled.

In addition, a uniform surface is a usual requirement for finished work whether that surface is dull or bright.

General Methods.—Thus the preliminary processes of polishing and cleaning are of the utmost importance. Such processes may be roughly grouped under two headings :—

1. Mechanical.
2. Chemical.

Mechanical processes include such operations as grinding, bobbing, sanding and polishing. These, in general, aim at the production of a uniform surface.

Chemical processes, with which may also be grouped some which are electro-chemical in that they employ the electric current, aim at the removal of grease and scale and the last traces of oxide tarnish, and attain the chemical cleanliness which is a *sine qua non* of good work.

Mechanical Cleaning.—We now consider the dry or mechanical processes.

The polishing of metals by various means has been practised from the earliest times, and surprisingly beautiful work has been achieved with the crudest implements. Time and competition were not then factors to be considered. In the rush of modern work time is an important factor, and work, which formerly may have taken days, must to-day needs be done in minutes.

The solid abrasive wheel of emery or other material, which may be natural or artificial and is united by some bonding material under pressure, is suitable only for rough work. It is used principally by ironfounders, brassfounders and engineers, whose work falls outside the category of cleaning metals for deposition and coloring.

The Sandblast.—One of the earliest operations in the dressing of metals is that of sandblasting, in which a stream of fine sand carried along in a current of air is allowed to impinge on the metal for one or other of several purposes. Thus the sandblast is used by the foundryman for removing the sand which adheres to the casting and also for removing sand cores. The metal finisher, however, employs the same principle to impart a dead—that is an evenly roughened—surface to work by way of contrast with some parts which are left bright and with a view to producing darkened colour effects.

A wide variety of sandblasting machines have been evolved since the principle was first embodied in a machine by Benjamin Chew Tilghmann in 1871. In one very common form the sand is sucked into the stream of air from a foot or power blower. Figs. 1 and 2 show two machines in common use, the former being operated by

foot and the latter by power. The action of the stream of sand is as follows : The sand particles are not necessarily harder than the surface of the material being treated,

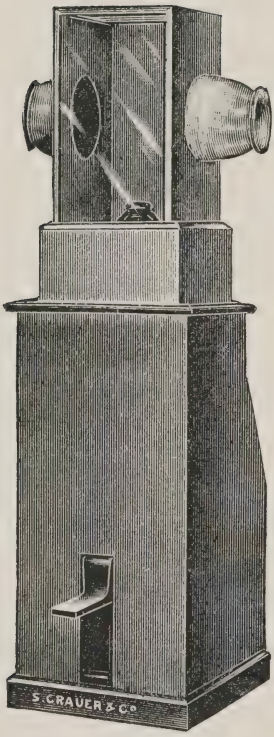

FIG. 1.—FOOT SAND-BLAST MACHINE.

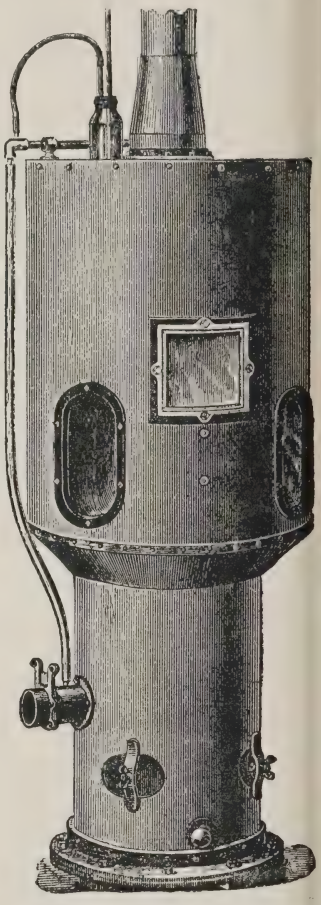

FIG. 2.—POWER SAND-BLAST MACHINE.

but their impact chips off fine particles from the material, though the sand particles may be broken in the operation. These chippings of the material are very small, and their

loss leads to a surface which is uniformly but not deeply roughened. The hardest substances such as glass are most amenable to sandblasting in that they suffer their particles to be chipped away rather than yield to the stream of sand. The metals are, as a rule, softer and more yielding, and are therefore less affected.

The process, however, serves admirably to produce the type of roughened surface which the artistic metal colorer will need. Articles are held in the hand over the jet from which the sand stream issues, and templates can be used with a view to sandblasting parts only of the surface of an article. Similarly, parts required to be kept bright may be stopped off by gummed paper, which is subsequently easily removed by wetting.

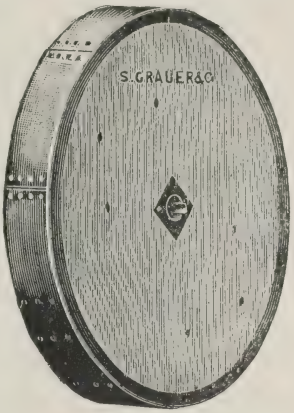

FIG. 3.
LEATHER-COVERED BOB.

Polishing Bobs.—The leather-covered wood bobs are made from selected wood having a cross-grain section. These are covered on the face with leather, which is either pegged or glued on (Fig. 3). The whole is then turned true and the leather face dressed with glue and rolled in emery and allowed to dry before using. The bob is thus of the nature of a continuous file. These bobs must run true on the spindle, otherwise they will not last long. Further, work cannot be well done on a badly running bob, and there is also the danger of injury through the leather strip becoming detached.

The leathers most largely used for this purpose are

seahorse or walrus and bull-neck. Hard bull-neck is used for sanding, and a softer grade for emery bobbing steel and iron in the cycle and motor trades. Their feature is their open texture, which is necessary for the retention of the emery which is applied to them. For sanding silver work a very soft leather is used, while bobs covered with buff leather are used only for jewellery work and then in only small sizes.

Very commonly to-day bobs are of solid leather. Discs of this material are firmly cemented together, and more recently these are giving place to solid felt discs which provide an excellent medium for retaining the polishing material. These solid leather and felt bobs may be turned up to any shape as required. The side bob is bevelled and can be used for polishing angles where ordinary bobs would be useless. The V-shaped bob is a useful tool, as is also the U-shape. There is then the hollow bob with a circumferential groove in various sizes to fit tubular work. Nick bobs are made from hard tanned leather and are used for sanding. The leather can be turned to any shape in the lathe with an ordinary wood chisel, but emery cannot be glued to the surface.

Dressing Bobs.—For this purpose only the best glue should be used, and the emery should be warmed before rolling on the glued bob. Better adhesion is thus obtained.

Redressing Bobs.—This is an even more important operation. After the bobs have been in use for some time, the surface loses its cutting power and the bob needs redressing. The surface is first cleaned off by revolving the bob and pressing against it a hard material, such as a medium hard builder's brick or a piece of lump pumice. This produces a clean surface free from dirt

and ready for a further application of glue and emery. The glue should not be so thin as to run like water, nor even of the consistency of treacle, but such as will allow it to flow with a brush and remain where it is put. The emery is contained in an iron tray with sloping ends. The bob is supported by an iron rod passing through its centre, enabling the bob to be rolled in the emery with a sufficient pressure to force the emery into the glued leather surface. The bob should thus be well and smoothly covered. It is set aside to dry and finished off in an oven. Before using, the edges are trimmed by placing an old file lightly against the sides while the bob revolves, and a similar application on the face for a moment or so will be sufficient to detach loose and protruding masses of emery.

While such bobs could be made by the operator, they are more preferably purchased from a well-known maker. Revolving at very high speeds, only the very best workmanship can be admitted, otherwise catastrophes are liable to occur.

Emery Tapes or Belts are very suitable for grinding and polishing work with curves. They may be used by hand, but are much more efficient when power driven (Fig. 4). The tapes may be obtained in various grades in rolls containing many yards, while machines and attachments can be procured ready for use. An arrangement which is simple and of easy construction may be described. Screw together two 8 ins. by 2 ins. bobs, making a pulley 8 ins. by 4 ins. This is fixed on an ordinary polishing-lathe spindle and must run as true as possible. In this pulley, turn out with a wood chisel a space $3\frac{1}{4}$ ins. wide, leaving a flange each

side $\frac{3}{4}$ in. by $\frac{3}{8}$ in. The emery tape runs in this groove and must run true. No wobbling is permissible. In a more satisfactory job the pulley would be fixed to the lathe spindle by a collar and nut, and will be less liable to run out of truth.

Another pulley is now required for the other end of the tape to run on. Two wood bobs 4 ins. by 2 ins. are

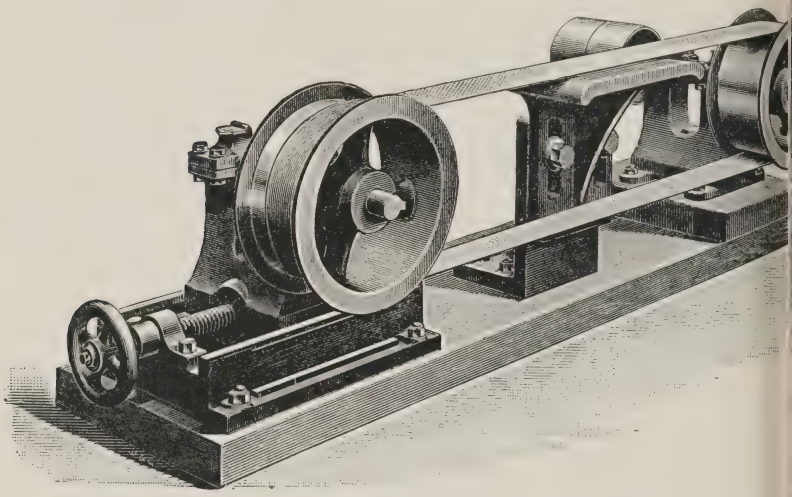

Fig. 4,—Emery Belt Polishing Machine.

screwed together and turned up in a lathe with a similar groove and flanges. Prior to turning up, a hole is bored through the centre large enough to take a $\frac{1}{2}$-in. tube fitting tightly. This is a friction bush to take the wear when revolving and must therefore be kept well oiled. This pulley is now run on a spindle which exactly fits the $\frac{1}{2}$-in. tube. To support the spindle, two oak brackets, each 12 ins. by 8 ins. by 3 ins., are provided, and one is bored with a hole to take the spindle as a driving fit. The holes do not go right through the brackets. The other

bracket is arranged so as to permit of taking off the emery band. To do this a hole is bored to take the end of the spindle as a snug but not driving fit. The end of the block farthest from the polishing lathe is cut away to the extent of 4 ins. by 5 ins. and a hole bored through the thinner part and a bolt fitted to form a swivel which allows the block to be swung on to or off the spindle. Another hole bored right through the 8-in. wood takes a coach screw into the bench to steady the running. It is removed when it becomes necessary to remove the emery band.

An adjustable tightener is an advantage. This may be made from a good sound piece of wood 12 ins. by 18 ins. by 2 ins. Four slots are cut, two at each end, 3 ins. long and $\frac{1}{2}$ in. wide to take coach screws $3\frac{1}{2}$ ins. by $\frac{1}{2}$ in. Under the heads of the coach screws place iron washers, or, better still, plates of iron $1\frac{1}{2}$ ins. sq. The whole is now bolted to the bench in such a position as to allow it to be pushed back enough to tighten the emery tape. The coach screws are then tightened down before running.

Stitched Mops.—These are used in the later stages of polishing. They consist of discs of soft materials such as calico, linen, swansdown or basil leather, bound together by a leather stock which screws on to the polishing spindle. These discs are stitched circularly. They are usually procurable in diameters from 1 in. to 18 ins. (Fig. 5).

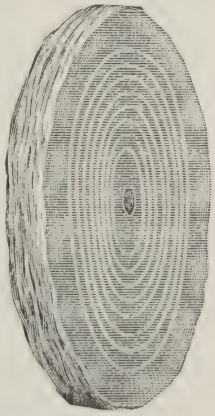

Fig. 5.
Stitched Mop.

Each of the above-mentioned

materials has its special uses. Calico mops are white and hard as compared with the grey cotton mops. The white calico mop is used for cutting down brass and solid nickel, and is fed with bar emery composition tripoli or crocus. This is a good serviceable mop.

The surface may be softened by pressing against it while running, a piece of perforated tinned iron with the rough side against the face of the mop. A mop dresser is shown in Fig. 6. This is then suitable for finishing

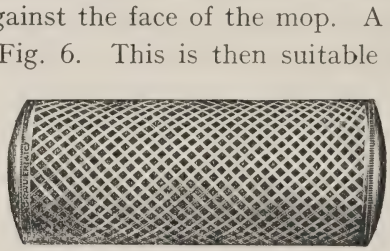

Fig. 6.—Mop Dresser.

nickel-plated work with tripoli, white compo or lime and tallow.

The grey cotton mop, being much softer, is very suitable for finishing silver, electroplate, tin ware and best finish brasswork. For a very high finish of good silver electroplate and copper the swansdown mop is used. This is made in two qualities, white which is very soft and a brown which is not so soft but more durable.

A stitched mop runs with a harder surface than one with loose discs, and is suitable for grease mopping (white variety) and for finishing (grey quality).

Basil leather mops are made from discs of the soft leather similarly mounted. These mops can be used on figured work on which they do not clog like calico mops. A good soft true-running basil leather mop makes a good coloring tool. A harder quality is made for sanding. These mops can be stitched or loose.

Chamois leather mops are still softer and are used for oloring gold, silver and nickel, especially in figured vork.

Circular Brushes.—Bristle and fibre brushes are used xtensively for metal polishing, the soft bristle brushes vith rouge for jewellers' work and the stiffer bristle and ibre brushes with rottonstone, emery and Trent sand. The fibre brush is largely used in the cycle and motor rades with flour emery mixed with oil as a finish previous o nickel plating.

Emery is a very well-known abrasive. Chemically it is natural form of aluminium oxide or alumina, but it ontains oxide of iron in amounts varying from 8 to 30 per cent. This oxide of iron has no abrasive value, but serves a useful bonding purpose when the emery is vorked up as vitrified wheels. The substance has been ised as an abrasive from the earliest times. It is now upplied in suitable sizes for all grades of work. The isual size numbers are 12, 18, 20, 24, 30, 36, 40, 46, 54, 60, 70, 80, 90, 100, 110, 120, 130 and 140. The smaller numbers represent the coarser grains. There are then lour emery, washed flour, double-washed flour and reble-washed flour emery. The coarse grades are used n engineering works and for ironwork in shaking barrels. Size 120 is used on bobs subsequent to size 90 and prior o flour emery brushing or glazing. High-class finishes are obtainable with the still finer grades, the washed flour being usually considered to be fine enough for a high-class finish on iron and steel.

Trent Sand is used for roughing out brass, nickel and ll solid white metals such as tableware for electro-leposition. Before using, the sand should be well sifted,

preferably through muslin or through fine sieves readily obtainable in diameters from 8 ins. to 16 ins.

Tripoli.—This is a silicious powder which consists of tiny skeletons. It is largely obtained from Tripoli. The best varieties are obtained from Corfu. While mainly composed of silica, it usually carries some alumina and oxide of iron. While sometimes used in the powder form with brushes or in burnishing, its most common method of application is in the form of a stiff paste with various greases and waxes, which are applied to the revolving mops during the polishing processes. It is graded so that, in some cases, a definitely cutting effect is produced, while polishing effects attend the use of the finer material. The grease and wax mixtures should be of such consistency that they cling to the mop, otherwise waste by disintegration occurs.

Crocus and Rouge are forms of oxide of iron. Usually they are made by heating ferrous sulphate (green vitriol) until all volatile matter has been expelled. Crocus is usually purple in color, while many variations occur in the color of rouge, probably due to slight variations in composition and method of manufacture. Both materials may be used as powders, pastes or compositions. The usual grades of rouge are "AA," extra superfine for high-class gold and silver work, "A," very fine, and "B," fine. Ordinary gold and silver work is finished with "A," while "B" is used for silver and high-class brass. Crocus is employed for lower-grade work and is a cheaper material than tripoli. Special methods of precipitation are used in the production of the finest grades of rouge. The finish obtained by rouge is frequently spoken of as "color," and this "coloring" must be clearly dis-

inguished from the chemical coloring which is to be liscussed later.

Lime.—Two varieties of lime, viz. Sheffield and Vienna, are extensively employed in the final "coloring" of nickel and brass. Vienna lime gives the finer finish, but is the much more expensive product.

Theory of Polishing.—The several stages through which a rough piece of metal attains a high polish are of considerable interest and are not without some influence on the practical side of the question. In the initial stages the grinding processes serve to detach prominent particles of metal and to produce a more or less level and uniformly scratched metal. In the finer stages of grinding still using such a cutting material as flour emery, the direction is changed and the deeper cuts are replaced by a uniform series of finer cuts, which to the eye begin to present the first real evidence of polish.

When, however, we change over to the use of soft mops with some form of polishing powder and running at high speeds, the action on the surface of the metal entirely changes. Here a layer of apparently mobile metal—metal in a more or less plastic condition—flows into and fills up the hollows, giving the smooth and highly polished effect. The fine scratches are not obliterated, and again become obvious when surface etching removes the film of metal which has been spread over the scratched surface. Further, it is highly probable that some of the polishing medium becomes inextricably mixed up with this surface layer of amorphous metal and then plays some part in the final "color" which is thus produced. The use of lime in the last stages of nickel finishing seems to be a case in point.

CHAPTER VI

CHEMICAL METHODS OF CLEANING METALS

Introduction.—After passing the various stages of mechanical preparation, metal surfaces are still far from attaining that super-cleanliness which is a *sine qua non* for successful electro-deposition and metal coloring. Such work may still carry films of tarnish in addition to grease, which has been employed in the polishing processes. Again, much work will not be amenable to many of these mechanical operations. Chemical methods must then be resorted to for the removal of such unwanted material as casting sand, oxides of metals and the various greases which may have been used for lubrication during machining operations or for subsequent protection from rusting.

When we use the term clean in connection with prepared work, the term carries a strictness of meaning not ordinarily imposed upon it. It does not mean clean as far as the naked eye is concerned, nor even is it cleanliness according to the microscope. It means absolute freedom from anything which prevents perfect adhesion between the molecules of superimposed material and those of the basis metal. If dirt is defined as "matter out of place," then many apparently clean and quite good-looking materials will have to come into this dirt category.

Types of Dirt.—Three chief types are to be noted: (1) mineral, such as the sands which adhere to a casting; (2) organic, comprising various greases, varnishes or paints which may have already been used upon the metal; and (3) films of metallic compounds which have resulted from the exposure of the metal to air during, and subsequent to, the work through which it passed in the process of manufacture.

Removal of Grease.—All metal work as it comes from the polishing operation or from the rolls carries films of grease. Successful deposition or metal coloring is impossible in the presence of such films of grease. Greasy materials are divisible into two classes: (1) vegetable and animal, and (2) mineral. They are chemically very different and require different methods for their removal.

Animal and vegetable fats and oils are insoluble in water, but are dissolved by hot potash or soda. With potash, which is commonly used, the soluble compounds formed are glycerine and potassium compounds of the "fatty acid." A very common constituent of animal fats is "stearin" or glyceryl stearate. Its composition is:—

$$C_3H_5(C_{17}H_{35}CO_2)_3$$

It is really a salt of glycerine (glycerol $-C_3H_5(OH)_3$) with stearic acid, $C_{17}H_{35}CO_2H$. Potash decomposes this stearin thus:—

$$C_3H_5(C_{17}H_{35}CO_2)_3 + 3KOH = \underset{\text{glycerol}}{C_3H_5(OH)_3} + 3\underset{\text{potassium stearate}}{C_{17}H_{35}CO_2K}$$

Potassium stearate is, in fact, "soft soap," and is of course soluble in water. Caustic soda is equally efficacious and gives sodium stearate, which is the main constituent of all hard soaps.

The potash bath contains :—

Caustic potash ½–1 lb. . .	50–100 grms.
Water 1 gall. . . .	1 litre

The potash used is American brown potash. It is a chea and suitable form, but has its limits in removing greas These are indicated by the above equation. The soa formed has of itself some grease-removing power, bu sooner or later, the bath requires renewing.

In the hot solution the work may be hung or scoure Freedom from grease is shown by water running evenl over the surface without showing the well-known tendenc to quickly leave portions of the surface.

All metals cannot be freely treated in potash. Neith aluminium nor zinc should be more than momentaril dipped in the solution. Both metals freely dissolve i KOH :—

$$Zn + 2KOH = K_2ZnO_2 + H_2$$
$$2Al + 6KOH = 2K_3AlO_3 + 3H_2$$

In each case hydrogen is freely evolved. Mops for scou ing with potash are of cotton for, while cotton is n attacked by it, bristle does not stand up against h potash. The potash solution is conveniently contain in an iron tank, and may be heated by a gas ring or ar other convenient method.

Alternative to potash, a strong solution of washi soda may be used, but this is by no means so effectiv

As the potash becomes impure, work passing throu it becomes stained, but such stains are readily remov in the subsequent treatment, and where this is not fort coming the stains may be removed by passing throu a 5 per cent solution of " cyanide."

Now potash has no chemical action upon mineral oi

Ordinarily they are not eliminated by potash. They may, however, be emulsified—that is broken up into very small globules which can be washed away—by a soap solution. The potash bath in use soon contains soap, and so mineral oils may also be removed in the potash bath.

The method, however, should not be relied upon for more than mere traces of mineral oil. Large quantities, that is if the work is decidedly greasy, should first be removed by immersing in, or rubbing with, a cloth moistened with a light oil, such as petrol or benzine. After wiping over with a rag, the last traces may be removed by potash.

Electrolytic Cleaning.—This is a method which has, in recent years, obtained a large vogue. It is in general suitable for removing grease, rust and scale in either acid or alkaline solutions. We are here concerned with the more particular case of the removal of grease. This is effected in the ordinary potash solution contained in an iron tank. The work is made the cathode and the tank anode and a heavy current passed. This process brings about a quick and complete elimination of grease and even scale.

The theory of the process has been much argued about, and the matter has not been greatly simplified by the fact that some operators use the connections in the opposite direction, that is, they make the work anode, while others even reverse the current during the process. Speaking generally, a suitable current is produced by an electric pressure of 6 volts across the bath.

A simple explanation of the process when the work is made cathode may be easily outlined. With the passage of current, electrically charged potassium atoms called

ions flow or migrate to the cathode. There they lose th charges and become changed into ordinary atoms, whi at once attack water thus :—

$$2K + 2H_2O = 2KOH + H_2$$

Both the products KOH and H assist in the cleanir The freshly produced potash attacks the saponifiable o and dissolves them. The hydrogen acts mechanical It is produced between the metal and the grease, and lifting away from the metal it disintegrates the grea film and so removes it. Conformable with experien unsaponifiable as well as saponifiable oils are remove and the hydrogen gas is even produced under films oxides and so removes them. This is a very simple vi of the process and must not be regarded as a complete satisfactory explanation.

Yet it must not be supposed that the process is appl able without limit. For some classes of work it is qu unsuitable, as the gases evolved markedly and det mentally influence the physical properties. This is t case with steel springs which become brittle.

As an alternative to the potash solution for electr cleaning, the following may be used :—

Caustic soda, 1 lb. . .	100 grms.
Soda ash, 1½ lb. . . .	150 ,,
Water, 1 gall. . . .	1 litre

Acid Dips.—After the removal of grease by means potash there then remains the task of removing the sta and oxide deposits which are to be found on all ty of manufactured articles. These may be mechanica removed by some method of scouring, using sand pumice powder, or even in some cases whiting or slak

me. Acids and other chemical substances, however, re very largely used. Their use is based on the fact that ıey dissolve either the oxide or the substance which ɔnstitutes the tarnish, or, what is much more usual, they issolve away the surface layer of the metal in preference ıd thus loosen the film of oxide which may also dissolve, r fall off, or be subsequently easily removed by some mple scouring process.

It will be obvious that the choice of dips will first be ıfluenced by the chemical nature of the metal or tarnish, ıd thus dips differ widely according to whether they are ɔ be used for copper, brass and similar coppery metals, nc and its alloys, lead and tin and their various com- ositions, or the several forms of iron or steel.

Again, when these oxide films are very stubborn, weak ɔids are allowed to act upon them for long periods. ıch weak acids are usually called "pickles," and the rocess "pickling."

Still further, the acids used for dipping may act upon ıe metal in several ways. Thus a very vigorous action ay lead to the production of a dull or "dead" surface the metal treated, while a variation of the composition the acid may quite restrain the action of the acid on ıe metal and thus yield a bright result. There are thus ead and bright dips in addition to those commonly used hen neither of these extreme conditions are specifically med at.

Dips for Brass.—For the plating and coloring trades mixed acid is commonly sold under the name of "dip- ng acid." This is a mixture of aqua fortis and oil of triol. The proportions are not very definite. Indeed, ey are open to some considerable variation. The

metal colorer may, however, mix his own dips. For general work the following well serves :—

Aqua fortis . . .	2½ lbs.
Oil of vitriol . . .	3 ,,
Common salt . . .	13 ozs.
Water	1 gallon.

The oil of vitriol is slowly added to the water with constant stirring, and when the mixture has cooled the aqua fortis may then be added and also the salt, with stirring. This dip will in course of time become less active. It may then he reactivated by the addition of more aqua fortis and salt. The dip, of course, accumulates copper and zinc salts, which sooner or later will separate out at the bottom of the acid-proof earthenware vessel containing the dip. Usually no advantage would accrue on the small scale in attempting to recover these. The spent dip, however, may be diluted down and used as a pickle for treating castings.

Bright Dip for Brass—

Aqua fortis . . .	1½ lbs.
Oil of vitriol . . .	2 ,,
Common salt . . .	10 grains

A **Whitening Dip** may be made from an old acid dip with the addition of 2½ per cent of common salt and 5 per cent soot. The process may be hastened by the addition of sulphuric acid, allowing the mixture to cool before use.

A **Finishing Dip** contains :—

Aqua fortis . .	100 parts by weight
Common salt .	1 ,, ,,
Soot . . .	1 ,, ,,

reviously dipped work is drained and passed through this ixture for a few seconds only. The dip acts vigorously. inse quickly and dry off. A fine lustre results, varying cording to the different type of alloy treated.

Dead Dips for Brass—

Aqua fortis . . .	$2\frac{1}{2}$ lbs.
Oil of vitriol . . .	$2\frac{1}{2}$,,
Common salt . . .	15 grains
Zinc sulphate . . .	20 ,,

By aqua fortis it may be assumed that a commercial itric acid of specific gravity 1·25 and containing 40 per ent HNO_3 is meant, while the usual oil of vitriol would ave a specific gravity of 1·7 and contain 70–80 per cent H_2SO_4. The foregoing acid dips are used only momenarily, and are followed by rinsing in an ample supply of lean water. Two or more successive immersions may be equired for difficult work. A patchy appearance is robably due to faulty pickling, and an even surface nay be restored by passing through a solution of zinc hloride, removing, heating until dry, rinsing, boiling in vater and drying out.

German Silver (an alloy of copper, zinc and nickel) nay as a rule be passed through the same acid treatment s copper and brass. The percentage of nickel in it does ot in any way interfere with the action of the acid on he copper and zinc constituents.

A good dead dip giving a rough crystalline finish imilar to that produced by sand blasting is obtained vith the following mixture :—

Aqua fortis (38%) . .	1 gall.
Oil of vitriol (66%) . .	1 ,,
Common salt . . .	6 ozs.
Water	$\frac{1}{2}$ gall.

Lead and Tin and their alloys, such as pewter and Britannia metal, are not usually treated with acids. Nitric acid does not dissolve tin, but coats it with a white insoluble hydrated oxide ($SnO_2 \cdot xH_2O$); while sulphuric acid forms insoluble lead sulphate ($PbSO_4$) on lead.

Potash readily removes the grease, and after scouring with sand or pumice the work should be ready for treatment, which usually consists of coating with copper from the cyanide solution before any attempt is made at coloring.

Alternatively, the work after potashing may be passed through a 10 per cent hydrochloric acid, and, after rinsing, may be scoured with sand or pumice, or scratch-brushed with a steel brush fed with a little pumice powder.

Dips for Iron and Steel.—Iron and steel work may be pickled in a weak acid, such as :—

Oil of vitriol . . .	$\frac{1}{2}$ lb.
Water	1 gall.

Scale will be loosened in 15–30 minutes, after which it can be removed by scouring. A somewhat stronger acid :—

Oil of vitriol . . .	1 lb.
Water	1 gall.

requires only a shorter immersion of the metal. Alternatively, work may be passed through both acids with an intermediate scouring, and such pickles and dips are essential in the case of work which, by reason of its shape or on account of a dead surface which may be required, is not ground with emery and polished.

As an alternative to oil of vitriol, muriatic acid may be employed of equal strength.

Cast Iron.—For cast iron, muriatic acid is generally used :—

Muriatic acid . . .	1 vol.
Water	1 ,,

followed by scouring. Hydrofluoric acid (HF) diluted with twenty times its volume of water may also be used. In this case, however, the acid, on account of its vigorous chemical action on glass, porcelain and stoneware, cannot be contained in vessels of these materials. Wood, or a lead-lined wood, may be used for this purpose. Care should be taken to avoid contact of this acid with the skin. This is very important where cuts or sores are present.

In the subsequent scouring of iron after acid treatment, the use of a little slaked lime with the sand or a brief immersion in dilute ammonia is advisable in order to extract and neutralise any trace of acid which may have adhered to the metal in any pits and thus escaped removal by washing. It is of the utmost importance that all traces of acid should be removed from iron and steel, otherwise a rapid corrosion of the metal is sure to ensue.

Small Work.—For pickling and dipping small work, perforated baskets of stoneware are commonly used. These may, however, be replaced by baskets of lighter construction of copper, brass or aluminium wire. While copper and brass are unaffected by potash, but dissolved by nitric acid, aluminium is, on the other hand, insoluble in nitric acid, but dissolved by potash. Aluminium is therefore suitable for nitric acid dipping, having the added advantages of lightness and durability, and the fact that the acid flows freely from its surface and does not cling to it.

Scouring.—The effects of dips and pickles are to dissolve away some surface impurities and to loosen others. The latter are then removed, usually by scouring with silver sand, pumice powder, whiting or lime. A usual form of scouring bench and rinsing trough is shown in Fig. 7. This is a two-compartment trough, usually lead-lined. A scouring board slides over both compartments.

Running water flows into one compartment. This is,

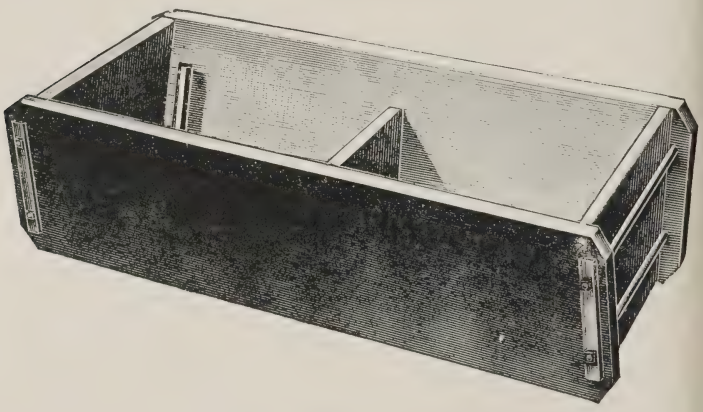

FIG. 7.—SCOURING BENCH AND RINSING TROUGH.

therefore, always clean and provides a final rinsing water. It then flows into the second compartment before passing to the waste. This second compartment is used for first rinsing. The need for a perfectly clean final rinsing water should need no further emphasis.

Scratch Brushes.—These are made of steel, brass and German silver wire, which may be straight or crimped. The wires are mounted in a wood stock, which is screwed on to the spindle. A number of these are shown in Fig. 8.

Steel wire brushes are used for very coarse work, such as castings and also for frosting. Fine steel wire brushes are used for gun-barrel finishing. Coarse wire brushes of brass are used by brass founders and others. Crimped brass wire brushes are suitable for gold work, finishing sand-blasted gold and silver, and producing a very dead finish upon silver goods. These are of very fine wire and can be obtained in several degrees of fineness. The speed of such brushes is about 2000 revs. per minute. Small diameter brushes should be run faster.

German silver wire scratch brushes are serviceable for coarse frosting before plating, while finishing is done with a fine brass wire scratch brush.

Other varieties of scratch brushes include the cup brush for the inside of cups, the case brush for card cases and match-boxes and the thimble brush. These are all very useful tools. Then there is the swing frosting brush with a speed not less than 1500 revs. per minute. Hand scratch brushes are made in several degrees of fineness, while wire scratch knots used in the grate and fender and lamp and chandelier industries are made of steel, brass and German silver wire of various grades of fineness.

FIG 8.
SCRATCH BRUSHES.

Burnishers.—Burnishers are made of steel, bloodstone or agate (forms of silica), in various sizes and patterns to suit the different types of work. Examples of these are shown in Figs. 9 and 10. Bloodstone and agate are rustless, while steel burnishers are sooner or later liable to rust, unless special care is taken with them.

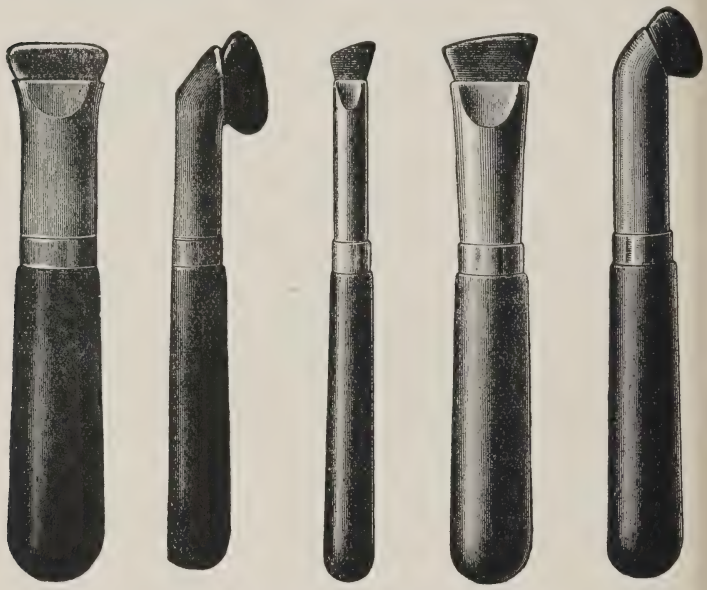

FIG. 9.—BLOODSTONE BURNISHERS.

The art of burnishing is chiefly in the hands of female workers, who, as a rule, have their own tools and religiously keep them in order, buffing them on a special buff from time to time and in every way taking the utmost care with them. The powder used on the burnishing buff is putty powder, which is purchasable in suitable tins provided with nozzles.

Work to be burnished is usually scratch-brushed after plating. The actual process of burnishing varies some-

what with different workers. A lubricant to allow of the easy motion of the tool over the work is used. Common substances used are soap and stale beer. This is contained in a convenient vessel and the burnishing tool dipped into it from time to time. The tool is held firmly in the right hand and applied to the work in a slanting position and with the necessary pressure. To-and-fro motion until the whole of the surface has been covered with steel burnishers, produces a certain degree of brightness and

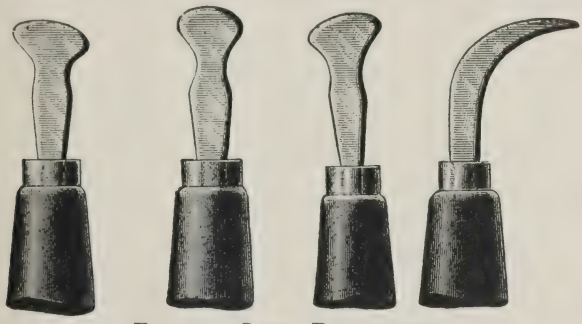

Fig. 10.—Steel Burnishers.

also compactness of the surface metal, this carrying with it a greater degree of endurance.

Steel burnishing is then followed by bloodstone or agate burnishing. This removes any marks left from the steel tools and imparts a greater degree of polish. Even after this treatment a finishing burnisher of great smoothness is frequently used.

Some operatives prefer to scour the surface prior to burnishing, using fine sand and soapy water. Others use 120 pumice and soapy water.

Burnishing is a special art. Operatives are taught when young, and experience alone brings perfection. It is even said that the best burnishers are " born burnishers."

Water-of-Ayr Stone is used by jewellers and silversmiths for removing scratches from gold and silver. The smooth stone is first dipped in water and rubbed in one direction, from end to end. Being a keen cutter, it soon removes scratches and pits. After this treatment the article is dried off by polishing with a soft leather with rottonstone or other fine polishing material mixed with oil. The soft leather may conveniently be fixed to a piece of wood by glueing.

Drying Out.—After the various processes of coloring, plating, or wet cleaning, work requires to be dried. It is essential that this operation should be completely and quickly done, otherwise stains and discolorations are liable. As to the method of drying out, there is little choice. Sawdust is practically the only material used for this purpose, and the work is either rubbed, shaken or barrelled with warm sawdust after passing through clean hot water. The usual type of sawdust " tin " is shown in Fig. 11, and is seen to be double bottomed, so that the sawdust can be heated, without fear of burning, by means of hot water. The immersion of the work in hot water should be long enough to allow it to become well heated. It is then quickly dried in warm sawdust.

There is some choice in the selection of the sawdust. Some woods are too hard and are likely to scratch the work. Others contain resinous materials which soften with the heat and adhere to the work. Some contain tannin which leads to discoloration. Practically the only two woods available are boxwood and maple. Both are largely used. They should be fine but not dusty, and should fall away from the work and not adhere to it.

Some attempts have been made to replace sawdust

drying by centrifugal machines which, rotating at a high speed, throw off the moisture. A further refinement is that of passing warm air through the machine.

Such machines may have a limited application for particular classes of work. They suffer the disadvantage that there is no relative motion of the individual pieces of work as in barrelling, and appreciable quantities of moisture may thus be retained by deep parts of figured work.

When the sawdust ceases to serve for drying out

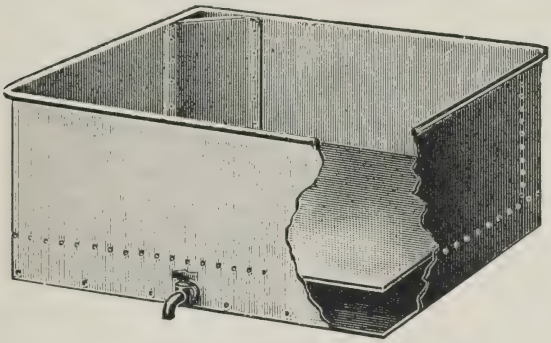

FIG. 11.—SAWDUST PAN.

finished work, it can still be used for the rough drying of work which has been cleaned with benzine or similar liquids until it becomes too impregnated with polishing materials. Before entirely scrapping it, it may be even then further used in tumbling operations.

Spotting Out.—This is a trouble which occurs mainly with cast metals. All castings are more or less porous, and the numerous cavities in the surface of the metal while too small to be discerned with the naked eye may be large enough to cause trouble on the finished work. In passing through pickling, plating and coloring

solutions, the pores retain the various liquids which are not easily washed out. After finishing the retained liquids chemically act on the metals and produce salts which appear as spots. Hence the term "spotting out." These salts are, in addition, deliquescent. They continually attract moisture and the disfiguring changes are continued.

Some method of prevention is essential. A good procedure is as follows: After passing through the solution in use, the work is alternately passed through clean cold and hot waters. This has the effect of opening and closing the pores, drawing in clean water and squeezing it out again. The pores are thus washed. The work is then passed through a solution of red argol (crude bitartrate of potassium) which neutralises traces of acid. It is again rinsed in cold and hot waters prior to drying for lacquering.

If the castings are very rough, and the cavities large enough to be seen with the naked eye, they may well be heated in a clean flame or over a coke fire and then plunged into water while hot. With such precautions spotting out may be largely, if not entirely, obviated. *Avoid boiling the work in potash or other alkaline solution.* Cleaning from grease may be effected by quickly scouring with hot potash and then with a mixture of whiting and slaked Sheffield lime.

Examples of Cleaning Processes.

Rough Brass Castings.—These are first pickled in the following mixture:—

Water	100 parts
Oil of vitriol . . .	10 ,,
Aqua fortis . . .	1 part
Muriatic acid . . .	1 ,,

The oil of vitriol is added slowly to the water with tirring and followed by the addition of the other acids. 'he mixture is well stirred and allowed to stand for one our. The castings may be left standing in this pickle rom one to four hours, after which they are rinsed, first n cold water and then through boiling water, taking the recautions mentioned above for the prevention of potting out.

Rough projections are next filed or ground off with a olid emery wheel, leaving a surface suitable for bobbing. Vith a 70 to 80 emery-felt bob the surface is "cut lown" and followed by a 120 emery bob. A 120 emery rease bob is next used. This is an emery bob made airly smooth by lightly pressing a flint or piece of hard teel against it while revolving in order to detach undue oughness. The bob is fed with tallow, mutton fat or a ommon quality of composite candle. Sanding is an lternative process to emery bobbing and may, in the pinion of the operator, be the better process. This gives a ine cut to the work, preparing it for the calico mop with ripoli composition which should eliminate all lines left y the emery. This finish may suffice for most cases of netal coloring, but further processes can be indulged in.

A soft mop charged with Sheffield lime or rouge serves o remove any grease left from the tripoli. This surface hould be adequate for all the usual processes of coloring.

Prior to coloring, however, it will pass through the otash and be lightly scoured with a mixture of :—

Whiting	3 parts
Slaked Sheffield lime . .	1 part

ut scouring with 120 pumice should suffice for most work.

A dead or matt surface may be produced in several ways, such as sandblasting, pickling, scratch-brushing with pumice powder and water, or with a frosting wire brush.

Cyanide Dip.—The final stage before coloring is that of passing the article through a cyanide dip to remove mere films of tarnish which would interfere with the coloring operation. The cyanide dip is :—

Potassium cyanide, $\frac{1}{2}$ lb. .	50 grms.
Water, 1 gall. . . .	1 litre

A poor grade of cyanide will be good enough for the process, which will be followed by thorough rinsing.

Scouring with Lime.—When lime is used either alone or in combination with other materials it has a somewhat injurious effect upon the hands. This can, however, be minimised by the addition of a small quantity of permanganate of potash to the lime.

CHAPTER VII

LACQUERING

Permanence of Metals.—There are few metals which will withstand ordinary atmospheric exposure without rapid tarnishing, and the colors, too, which are produced by the methods to be described, while they are more stable than the metals upon which they are formed, are, nevertheless, sooner or later visibly affected by one or more of the corrosive constituents of any domestic or industrial atmosphere. Indeed, they could only be expected to retain their original lustre and color by very careful control of the conditions of exposure.

Greater permanence is therefore imparted in most cases by coating with a thin layer of material which may be bright or dull, colored or transparent, but which in the first case effectively prevents contact between the air and the metal.

Lacquers are liquids which are applied to metals for this purpose. They are solutions of materials in volatile solvents and, when applied by dipping, spraying or brushing, the solvent evaporates off, leaving the required thin protective film. Such films may also act as vehicles for imparting various shades of color, either to the plain or polished metal or to the chemical color produced thereon.

Lacquers of a wide variety can be purchased to suit any class of work. Transparent lacquers are used on silver-plated work, and, indeed, for any example where

it is not required to add color to the existing surface. Of the colored lacquers, pale gold is used for a large amount of brasswork.

Gold is chiefly in demand for brass fittings, and deep gold is used largely on scientific appliances. There are also numerous shades, such as amber, green, steel-blue, copper-tint, black and many others. All lacquers tend to thicken by the exposure which is unavoidable in their use. They then require the addition of further quantities of the solvent, and these liquids are termed "thinners." With them, too, it is possible to reduce the color of the lacquer. Thus a deep gold lacquer could be toned down to much paler shades.

It should, however, be noted that "rainbow tints" may be avoided by the use of colorless lacquers for toning down. If thinner only is used the lacquer loses body and becomes too thin. The colorless lacquer should, however, be of the same brand, and thinner only used to "cut down" to a working consistency.

While many lacquers leave a glossy surface, such an effect is by no means always desirable. In fact, a highly lustrous lacquer may completely spoil artistic effects produced by the various coloring processes, and may impart a very artificial look quite out of keeping with the aim of the artist. There are, therefore, dead lacquers—free from gloss.

Lacquers may be applied by one or other of three methods: (1) dipping, (2) spraying and (3) application with a brush. Again, some lacquers are best applied to warm work and subsequently stoved at a moderate temperature. Others are applied cold and are allowed to dry and harden with little or no elevation of tempera-

ture. General indications as to the most suitable method of application will be given, but it will be obvious that some large work may not be easily treated by dipping, while small and cheap work could only be got through by the immersion method.

Preparation of Work.—In any case, the utmost care must be taken in the preparation of the surfaces to be lacquered. Grease and dust must be entirely absent, otherwise the finish will be seriously impaired.

Tools.—The tools required are chiefly camel-hair brushes of good quality. *Of good quality* must be emphasised! Common brushes are worse than useless. Good qualities are usually obtainable from lacquer merchants and platers' sundries houses. Suitable brushes are round or dome-shaped in several sizes, or flat in all sizes from $\frac{1}{2}$ in. to 3 ins. in width and from $\frac{3}{25}$ in. to $\frac{9}{25}$ in. in thickness. Fitch-hair brushes suitable for cold lacquering can be obtained in twelve or more sizes. They are usually dome-shaped and are usable on nearly all surfaces.

A lacquer basin is also very desirable. This is an enamelled cast-iron basin to contain the lacquer, with a wire across, over which the brush, charged with lacquer, is drawn to remove superfluous lacquer. Two examples are shown in Fig. 12. Lacquering stoves, for use in hot lacquering, may consist of closed ovens or merely hot plates. Fig. 13 shows a hot plate. The heat is usually supplied by atmospheric burners, but the construction is such that the burner gases do not come into contact with the lacquered work.

The selected lacquer is poured into the basin, avoiding excess. More can easily be added if required, while an

excess may mean waste, as it is bad practice to pour excess of lacquer back into the bottle. The basin may be cleaned with methylated spirit or hot potash, and thus left ready for further use.

Lacquer must not be left to dry and harden in the basin. Brushes, too, should be cleaned with methylated spirit or thinner, and wiped so that they will dry without clogging, and remain soft and smooth. Too often repeated cleaning should be avoided. During the course of a day's use the lacquer brush may be kept soft by being immersed in the

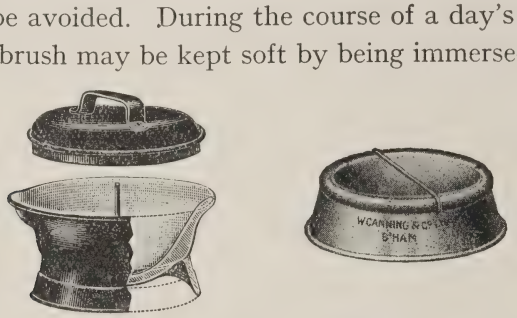

FIG. 12.—LACQUERING BASINS.

lacquer contained in a short wide-necked bottle provided with a stopper. The shaft of the brush fits through a hole in this stopper. When the brush is to be used the stopper is removed from it. Further, an easily fitted piece of wire can be stretched across the mouth of the bottle as a means of removing superfluous lacquer. This, too, can be made to unfasten when the bottle is to be stoppered.

Cold Lacquering.—The process may perhaps be best described by considering a few concrete cases. Take, for example, a brass tube, say 3 ft. long and 2 ins. in diameter. It has been polished and a good finish given to it lengthwise. It is dried off with Sheffield or Vienna lime. Some polishers, however, prefer rouge. The tube is now rubbed lengthwise with a soft dry leather or cloth

free from grit. The tube is placed on a peg projecting from the edge of the bench and a similar peg inserted in the other end for ease in handling. Such a length of tube should be manipulated without the help of an assistant. The required lacquer is poured into the basin and a No. 6 lacquer brush is dipped into it and then drawn across the wire. Starting at one end, the brush is drawn lengthwise along the tube, turning this round so that every part is covered. Sufficient pressure is required to ensure an even distribution of the lacquer and to avoid the forma-

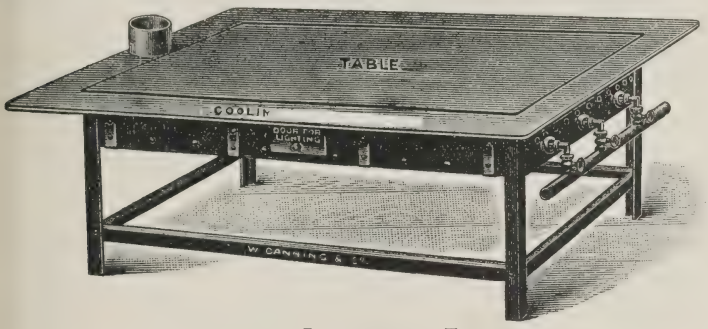

FIG. 13.—LACQUERING TABLE.

tion of " runs " or air bubbles. The tube is now examined, and, if the work is satisfactory, the lacquer is allowed to dry. Some manipulative skill is required and may with a little practice soon be acquired. Should, however, some early attempts prove unsuccessful, the lacquer may be removed easily before it is allowed to dry, by means of methylated spirit applied by means of a rag. Potash should not be used for removing lacquer. It often causes spotting. Methylated spirit produces no discoloration. The work should then be remopped before relacquering.

As another example, take a piece of figured work such as an ornamental lamp-stand. The final preparation in

such work needs special care, as it is extremely important that no "compo" should remain in any of the crevices or holes. Go over the whole of the article carefully with a dusting brush. Holding the article in the left hand and in such a manner that the hand will not come into contact with any part of the lacquered surface, apply the lacquer with the brush, working downwards from the top and continually turning the article round to bring a fresh surface under the brush. Let the lacquer flow freely and work it well into every part. Pick off the runs and air bubbles quickly with light strokes of the brush, and any excess which is retained in hollows is removed by the tip of a small-pointed brush. Fitch-hair brushes are best for applying lacquer to figured work. The work is then set aside to dry and harden in an atmosphere free from dust.

As a third example, take a plain flat surface highly finished, such as a brass tray about 12 ins. by 9 ins. After brushing free from dust, the tray is held in a slanting position at an angle of about 45 degrees. A broad flat brush, say, $1\frac{1}{2}$ ins. wide, of good fitch is selected. It is passed through the lacquer in the basin and across the wire, and then applied with a masterful stroke lengthwise along the tray. A slight bend on the end of the brush will indicate a sufficient pressure to ensure an even layer, while excessive pressure will squeeze out the lacquer into ridges at the sides of the brush. Such ridges, if they do occur, must be quickly levelled off. The operation is continued until the whole of the tray is covered with lacquer, and smart yet light touches are required to remove bubbles and streaks. In a successful job the surface will be as smooth as the metal beneath.

The beginner would do well to practise upon small pieces of metal of different shapes with a pale tinted lacquer, working up to larger pieces and with deeper shades. Considerably more experience is required for success with deep gold lacquers.

It is an advantage to harden off all cold lacquered work in a stove if possible, at a temperature of 100° F., for about half an hour.

Hot Lacquering.—For hot lacquering somewhat more elaborate apparatus is required than in the case of cold lacquering. The chief item is the stove.

A lacquering stove is made of wrought iron throughout, with a flat surface heated beneath by means of gas, which is clean and capable of very easy regulation. Other means of heating may be adopted, but if smoky fuels should be used it is very essential that the flue leading off the waste gases should be carried out of the room to avoid any possible chance of soot or other dirt falling upon the lacquered work. While gas heating is the best type of combustion heating, the electric stove constitutes the ideal method of heating. It is absolutely clean, and is capable of the finest regulation.

Special brushes are desirable for hot lacquering. When ordering brushes it should be stipulated that they are to be used for hot work.

Lacquer for the hot process may be obtained in about fifteen different shades, from which many intermediate shades may be made up to suit any class of work. The hot process produces lacquers which are very hard and not easily scratched.

As an example, take a tube of brass. This is highly polished, free from grease and dust. It is placed on the

stove until it attains such a temperature that it can be just comfortably handled. Having the lacquer ready, it is applied to the tube, which is held in a convenient position, with long strokes, turning the tube to expose all parts to the process. With a little practice confidence in this operation is soon acquired. If the lacquer shows signs of cloudiness, a few seconds on the stove will put it right. The whole operation is more difficult than cold lacquering, but the result is one which will withstand considerable wear and handling.

The beginner is again advised to try small pieces first so as to acquire experience before attempting a larger job. In some cases the lacquer may best be applied by means of a wad of cotton-wool dipped in the lacquer and then quickly drawn along the surface.

For figured work, the method then follows that given for cold lacquers as regards smart manipulation. Some lacquerers prefer French hot lacquers, and these are usually obtainable to order, and as a rule any special instructions as to the method of use are sent out by the makers of the lacquer.

Composition of Lacquers.—While it is assumed that most metal colorers will purchase their lacquers, some brief notes regarding the composition of lacquers may not be out of place. The art of lacquering, especially with colored lacquers, has been practised by the Chinese and Japanese for a long time. They used the oils and gums which exuded from many of their native trees. The lacquers of to-day are mixtures containing two essential constituents. The substance of the lacquer which provides the final hard covering may be a natural gum, or quite commonly a chemically manufactured product. To

uniformly spread such materials necessitates their solution, and solvents are therefore required.

Of the covering materials there are two chief examples. There are (1) the natural gums and resins, and (2) the chemical material called pyroxylin, which is made by treating some form of cellulose, such as cotton-wool, with a mixture of sulphuric and nitric acids. The gums and resins dissolved in alcohol produce spirit lacquers. Some resins, however, are harder and require to be dissolved in amyl acetate (pear oil) or amyl alcohol. Of these gums and resins may be mentioned shellac, copal, sandarac, mastic and damar. The solvents employed are alcohol and amyl acetate, either separately or in mixtures. A usual lacquer contains shellac in alcohol. Dyes may be added to impart color. Such lacquers are usually applied by the hot process.

Pyroxylin lacquers contain this substance dissolved in amyl acetate. Amyl acetate is expensive and may often be diluted with cheaper materials, such as benzine. Lacquers as sent out may be too thick for use and require some dilution with the same solvent. This solvent is called "thinner." As the solvents are volatile, the lacquers thicken by exposure and evaporation. They can then be reduced to a proper working consistency by the addition of thinner. Excessive thinning produces a lacquer which will fail, on drying, to retain strength, and will further show some signs of iridescence. This may, however, be rectified by the addition of a little more unthinned lacquer. These pyroxylin lacquers are usually applied cold, and are dried off by placing in a warm position.

Again, lacquers containing both pyroxylin and resins

are in wide use, and the mixing of these two main constituents adds the advantages of each and widens the range of variation for different classes of work. By mixing further with colored pigments and metal powders they may be applied in many cases of ornamentation apart from mere protection.

Lacquering Notes.—Where lacquer dips are in use care should be taken that no piece of work should be allowed to lie at the bottom of the dip vessel, for it will assuredly spoil the color of the lacquer. Two common constituents of lacquers are nitro-cotton and amyl acetate. Nitro-cotton is made by treating clean cotton with a warm mixture of nitric and sulphuric acids. The acids are then very carefully washed out from the product. But the cotton is cellular and perfect washing is exceedingly difficult, though absolutely necessary in the production of guncotton explosives. Thus a little sulphuric and nitric acids may occur in the lacquer and will attack metal exposed for any length of time.

Again, amyl acetate is a somewhat unstable substance. In the presence of a trace of moisture it decomposes, setting free acetic acid thus :—

$$C_5H_{11}\cdot C_2H_3O_2 + H_2O = C_5H_{11}OH + H\cdot C_2H_3O_2$$

It will be readily appreciated that this acid acting on copper and allied metals will produce compounds which will discolor the lacquer.

For this reason the lacquer containers cannot be of copper or brass. They may be of tinned iron if the iron is well tinned. Enamelled iron is preferable, but the best containers will be of glass or porcelain. Galvanised iron

ontainers are quite impossible, as electrolytic action ;ould be set up at any spots of exposed iron or adherent ietallic dirt. Wood containers cannot be used for olorless lacquers, which may deteriorate by dissolving oloring matters from the wood.

From time to time the lacquer should be poured off, he sediment thrown away and the lacquer strained back nto the cleaned vessel.

A fine nickel gauze suspended in the lacquer will serve o prevent detached articles from falling to the bottom, nd will also collect the larger particles of dirt.

Lacquers should be stored in a cool place, as warmth vill promote their decomposition.

Water Dip Lacquer and Wet Lacquering.—While most isually work is thoroughly dried before lacquering, it will e obvious that in the case of small work this offers some lifficulty, especially on account of the difficulty of re-noving sawdust from the crevices. This sawdust floats ff into the lacquer and spoils the finish.

This is obviated by what is called wet lacquering, in vhich the article after thorough cleaning, finishing and insing is passed straight into the dip lacquer without in ny way affecting the metallic finish.

Objections might at once be raised to the process. In he first place, it might seem impossible to wash away he water by means of the lacquer in which, with amyl cetate as its chief constituent, water is insoluble. econdly, trouble would appear to arise from the acetic cid which the water sets free. Nevertheless, the process s in extended and successful use. As a fair amount of vater is introduced into the lacquer, it falls to the bottom f the lacquer vessel and removes the bulk of the acetic

acid with it. But steps must be taken to draw off the water from time to time.

For the lacquer container a vessel of well tinned or enamelled iron will serve. A slightly sloping bottom and a tap will serve to drain off the water as it accumulates. Other methods will suggest themselves. A glass tube at the bottom with a stop-cock would give some indication of the end of the drawing off process.

For wet lacquering it is essential that the work should be passed into the lacquer before any tarnishing can occur. The lacquers used are thinner than those for brush work. They should not contain alcohol, as this would be washed out by the water.

Alternatively the wet work may be passed first through thinner and then on to the lacquer. The water is more quickly washed off by the thinner and settles more rapidly therefrom. In any case, thinner has to be added to the lacquer and may as well go in this way as by direct pouring in.

CHAPTER VIII

ELECTRO-DEPOSITION OF METALS

Introduction.—As will subsequently be seen, the range of chemical coloring processes on metals can be considerably extended by the prior application of comparatively thin films of other metals. In fact, the metal colorer's plant will naturally include the apparatus and materials required for the electro-deposition of such metals as copper, silver, gold, nickel, tin, lead and other metals. The metal colorer, too, has usually a passing acquaintance with these processes. Something more than a passing acquaintance, however, is necessary if work of a satisfactory order is to be turned out, if, as will certainly be the case, the final color effects are the result of chemical actions in which the deposited metals take part.

In this chapter, therefore, a brief outline of these processes will be given. Space necessitates only a brief treatment. A more detailed knowledge can, however, be acquired by reference to well-known works upon the subject. It is, however, generally assumed that the metal colorer will have some practical experience of the several operations in the deposition of metals, so that the chief points in each case only are touched upon. The literature on electro-deposition now includes a number of excellent books to which reference should be made.

Arrangement of Apparatus.—Sources of current may

include the dynamo, accumulators or primary cells. Seldom are primary cells now used. Depositing vats may be of wood, or wood lead-lined, stoneware, glass, enamelled cast iron or wrought iron. They may be obtained in a wide range of sizes. Some are definitely intended for use with cold solutions, while others are for warm solutions. Anodes (+) are of the metal to be plated. They may be cast or rolled, usually flat, but other shapes are sometimes used. A number may be suspended on a bar or rod of copper or brass, which is connected directly or indirectly to the positive terminal of the generator D. From a similar bar conveniently situated the work is suspended. This is called the cathode (−) bar, and is connected directly or indirectly to the negative terminal of the generator. The plating circuit should include an ammeter A to register the current in use, while a voltmeter V is put across the plating bath, that is, connected to the anode and cathode bars. Two alternative arrangements, both embodying this principle, are shown in Fig. 14. These also include a rheostat R, generally in the form of coils of wire, through some or all of which the current passes. This provides one method of regulating the current to the varied amounts of work in the bath.

Choice of Plating Solutions.—Plating solutions are required to meet a number of important conditions. They should be of simple composition and easy preparation. There should be no constituent without a definite purpose. Even small amounts of impurities may produce results out of all proportion to the quantities present. Occasionally very small additions produce highly beneficial results, but even these so-called "addition agents"

must be used intelligently. The main constituents of solutions must be stable compounds, unaffected by air or by the metals which will be immersed in them to receive a deposit. On this account silver nitrate solution is not used for plating. It is decomposed by many metals, while the double cyanide with potassium ($AgCN \cdot KCN$) is much more stable. Practically all iron solutions are affected by the air, and so also is the free cyanide in every cyanide solution.

Plating solutions should be good conductors. Copper sulphate is a poor conductor, and sulphuric acid is added chiefly to impart conductance. "Free cyanide" is not

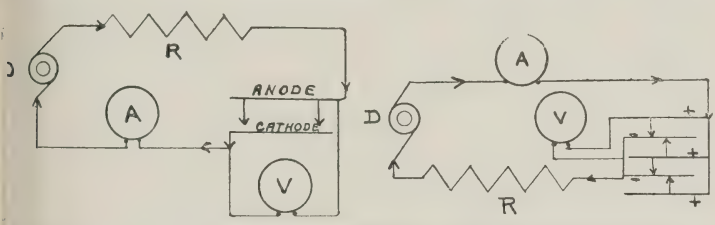

Fig. 14.—Arrangement of Essential Plating Apparatus.

so valuable in this respect. Its benefit lies in the prevention of the formation of insoluble and insulating films on the anodes. Most cyanide solutions are used at a temperature of 50–60° C. A nickel bath may not contain an appreciable amount of acid. Hence, conductors such as common salt and ammonium chloride are common additions. It is an advantage, too, if a plating solution contains a cleansing material, such as acid or free cyanide. These materials remove films of tarnish which unavoidably form subsequently to the final cleaning operation. Nickel solutions contain no such cleansing constituent, and, while not in any sense relying on the cleansing

properties of a solution, especial care must be taken with work which is being prepared for the nickel bath. Films of tarnish militate against adhesion of the deposits.

Few solutions may embody all these desirable properties, but every attempt will be made to, as far as possible, ensure their presence.

P.D.'s Required for Deposition.—When it is stated that plating solutions may be prepared and used under conditions which are in a measure not very definite, it becomes difficult to give exact figures for guidance. This is especially the case in the P.D.'s required for deposition. These are frequently stated with a precision which suggests exactitude in operation. Such, however, is not the case in practice. The values depend upon widely varying conditions. They will be influenced by temperature, strength of solution, presence of conducting compounds, and the distance between the electrodes (anodes and cathodes). Rigid figures, therefore, cannot be given. They may, however, be determined under the best conditions attainable, and may then serve as a good guide in subsequent work. With these provisos the following table may be given :—

P.D.'s Required for Ordinary Plating Solutions

Solution.	P.D.(volts).
Copper (acid bath)	·5–1·0
,, (cyanide bath)	2–3
Brassing	3–5
Silver	1–2
Gold	1·0
Nickel	2–3
Lead	1–2
Iron	2

It must be clearly remembered that these figures will be obtained on a voltmeter connected directly across the bath and not across the dynamo terminals or other source of current.

Current Density (C.D.).—By this term is understood the current passing on to unit area of cathode surface. The common method of representation is in terms of amperes per square foot. Thus a current of 3 amperes on one side of a cathode measuring 4×3 ins. represents :—

$$\frac{144 \times 3}{(4 \times 3)} = 36 \text{ amperes per sq. ft.}$$

In every case of deposition there are limits to the rate of deposition. Near and beyond them, rough and powdery metals are produced. The metal colorer will usually require deposits as smooth as possible. These in general will be obtained with low C.D., but the figure will vary with the concentration of the solution and whether it is at rest or in motion. The desirable figures for each metal will be referred to under their particular sections.

Rates of Deposition of Metals.—Faraday, in 1835, enunciated the law that metals are deposited under ideal conditions proportionally to their chemical equivalents. This is as would be expected. Now unit current (or rate of flow of electricity) is called the ampere, and is that invarying current which in one hour deposits, under these ideal conditions, 4·024 grms. of silver. The quantity deposited by 1 coulomb (that is, 1 ampere for 1 second) is therefore ·001118 grm. These ideal quantities are seldom exactly obtained in practice.

The accompanying table gives some useful data con-

cerning the weights of metal which may be deposited from some of the simple plating solutions :—

A Metal	B Symbol	C Chemical Equivalent	D E.C.E. m.gm.	E Grms. per amp. hr.	F lbs. (avoir.) per 1000 amp. hr.	G Mils per hr. per 10 amp. per sq. ft.
Copper (ic)	Cu	31·8	·329	1·183	2·61	·56
,, (ous)	Cu	63·6	·658	2·37	5·22	1·12
Gold .	Au	197	2·03	7·31	235 ozs. troy	—
Iron .	Fe	28	·29	1·044	2·3	—
Nickel .	Ni	29·5	·305	1·098	2·42	·575
Lead .	Pb	103·5	1·071	3·86	8·51	1·45
Silver .	Ag	108	1·118	4·024	129 ozs. troy	—
Tin .	Sn	59·5	·615	2·21	4·87	1·28
Zinc .	Zn	32·5	·338	1·22	2·69	·74

Notes.—Column A. Copper in the usual acid bath is in the cupr*ic* condition, while the cyanide solution contains cupr*ous* copper. The figures for gold are those for cyanide compounds, while for tin they are for stannous compounds.

Column C. Chemical equivalents are either the atomic weights or some simple sub-multiple.

Column D. E.C.E. means electro-chemical equivalents, or the quantities (here expressed as milligrams) deposited by 1 coulomb, that is, by 1 ampere in 1 second.

Columns E and F. Useful figures.

Column G. 1 mil. $= \frac{1}{1000}$ inch.

Deposition of Copper.—Copper is by far the most widely deposited metal, and for this purpose two solutions are in common use :—

(*a*) The acid copper bath, and
(*b*) The copper cyanide bath.

Each has its special advantages, applications and limita-

tions. The former is used in all cases of thick deposition, while the latter is limited to the deposition of comparatively thin films of the metal upon such base metals as iron, zinc, lead and tin and their alloys. As soon, however, as these metals are covered with an adherent and continuous deposit of copper, they are transferred, after thorough rinsing and possibly scouring or scratch-brushing, to the acid bath to acquire any necessary thickness of the metal.

The Acid Copper Bath.—The composition of this solution admits of some elasticity, but a good solution with a wide range of application is :—

Copper sulphate (bluestone),	2 lbs.	200 grms.
Sulphuric acid . .	6–8 ozs.	40–50 ,,
Water, up to . .	1 gal.	1 litre

Sometimes, minute additions of glue, gelatine or tannic acid are made with a view to giving a somewhat smoother deposit. The solution is a good conductor and is used cold, being commonly contained in wood vats which are lead lined. With a good copper anode, preferably electrolytic, the solution maintains its composition over long periods, and this admits of prolonged working under uniform conditions.

The solution is at once suitable for the deposition of copper upon copper, silver in special cases, brass and German silver. The base metals, such as iron, tin, and zinc and the lead and tin alloys, are attacked by the acid of the solution and must therefore be first coppered in the cyanide solution given below.

The electrical conditions for working the acid bath refer mainly to the P.D. (potential difference, volts)

between the anode and cathode and the current density (C.D.) on the cathode or work in amperes per square foot. Hence the need of both ammeter and voltmeter fitted as already shown in Fig. 14. In general work the C.D. may not exceed 30 amperes per square foot. Beyond this rate of deposition the deposits may, and with still higher C.D's certainly will, become dark, powdery and useless. In special cases of deposition the C.D., and with it the rate of deposition of the metal, can be appreciably increased by stirring the solution or keeping the work in motion. Such methods are commonly used. For the type of deposit which the metal colorer will require the C.D. should not exceed 20 to 25 amperes per sq. ft. The P.D. can only be less exactly stated. It is very variable with a number of varying conditions. It decreases with (1) stronger solutions, (2) greater acidity, (3) increased temperature, (4) reduced C.D. and (5) reduced inter-electrode distance. Much depends upon this last condition, the distance between the anode and work. With flat work this may be small, and a P.D. of ·5 to 1 volt may suffice. The figure should be carefully obtained by experiment and used as a guide in future work.

The Cyanide Copper Bath.—This solution should contain about 4 ozs. of the metal per gal. (25 grms. per litre). It may be prepared by several methods, two of which will now be outlined.

1. Copper sulphate (1 lb. for every gal. of final solution corresponds to 4 ozs. of the metal per gal.) is dissolved in water (about one-third of the volume of the final solution). Strong ammonia solution (·880) is added with shaking until the green precipitate (copper

hydrate) first formed is just redissolved to a clear deep blue solution. Potassium cyanide (about one and a quarter times the amount of copper sulphate used) is dissolved to a strong solution, which is now added to the blue copper solution until the blue color just disappears. This will take about three-quarters of the cyanide solution. The remainder is added for "free cyanide" without which the anodes cannot be kept clean during deposition nor can the current be kept constant. The solution will still probably be less than a gallon and must now be diluted with water to this volume. The following are approximate quantities for a gallon of solution:—

Copper sulphate . . .	1 lb.
Ammonia solution, ·880 .	16 fl. ozs.
Potassium cyanide . .	1¼ lbs.

Alternatively:—

2. Prepare a solution of potassium cyanide containing 1¼ lbs. of the salt per gal. Set aside one-quarter of this solution. Warm the remainder and add, a little at a time, green copper carbonate. At first it dissolves quickly; subsequently it goes more slowly. When no more carbonate will dissolve and its green color persists, cease its addition, and now add the cyanide solution first set aside. Any little excess of copper carbonate is quickly dissolved and, on warming, the solution is ready for use.

The quantities for one gallon will be:—

Potassium cyanide . .	1¼ lbs.
Copper carbonate . .	10 ozs.

These solutions should be worked warm (about 120° F.) with a copper anode. A P.D. across the bath of 2–3 volts

should suffice to give a good deposit on work which has been adequately cleaned.

In any case only thin films of copper are required from this solution, but they must be continuous. The work may then be rinsed, scoured or scratch-brushed, rinsed again and transferred to the "acid" bath for a thicker deposit.

Chevreul's Solution.—Without doubt the best solution for cyanide coppering is a solution of Chevreul's salt in potassium cyanide. This is a red compound obtained by mixing hot solutions of copper sulphate and sodium sulphite (Na_2SO_3). This "red precipitate" has a formula $CuSO_3 \cdot Cu_2SO_3 \cdot 2H_2O$, and contains 49·3 per cent of the metal copper. From

Copper sulphate . . .	1 lb.
Sodium sulphite . . .	$1\frac{3}{4}$ lbs.

about $8\frac{1}{2}$ ozs. of red compound are obtained. This "red copper," as it is sometimes called, may be washed and dried, or it may be preserved wet. It is readily soluble in potassium cyanide, some sulphur dioxide (SO_2) being evolved. Quantities for 1 gal. of solution are :—

Chevreul's salt	$4\frac{1}{2}$ ozs.
Potassium cyanide . .	7 ,,
Water	1 gal.

The red salt may also be purchased, and then only needs dissolving in the cyanide solution.

The solution is worked hot—about 120° F.—with a current of 3–4 amperes per sq. ft. It gives a good-colored smooth deposit, due undoubtedly to the combined SO_2 which it contains. The addition of various

sulphites to the ordinary cyanide bath is attended by improved results.

Electro-deposition of Brass.—Many base metals which are ordinarily not amenable to metal coloring, may be brought within the wide range of colors obtainable upon brass if they can first easily receive a coating of this alloy.

Any attempt at obtaining a brass deposit by passing a current through a solution containing any zinc and copper compounds would be quite useless. As a matter of fact, these would rather provide a method of separating the two metals. If a little nitric acid is added to the mixed copper and zinc sulphate solution and an insoluble anode such as lead or platinum used, the deposit would consist wholly of copper, so long as this metal remained in the solution. These conditions make for separation rather than for simultaneous deposition. The principle is employed in analysis.

For the deposition of brass, other conditions must be sought, and they are met in a mixed solution of copper and zinc cyanides in an excess of potassium cyanide. Briefly, it may be stated that an electro-brassing solution is prepared on the lines of the cyanide copper bath. Usually one-half of the copper compounds are replaced by similar zinc compounds. Each metal may be present to the extent of 2–3 ozs. per gal. Referring to the method given on page 102, the dissolved mixed sulphates are converted to the ammoniacal solutions. The zinc compound is colorless, but the blue color of the copper compound provides a guide in the process. The blue solution is decolorised by the addition of "cyanide" with an excess for free cyanide.

Alternatively, the equally mixed carbonates of zinc

and copper may be added to a cyanide solution to saturation and free cyanide then added.

From such a solution brass of 66 copper and 34 zinc, or thereabouts, is readily deposited, owing to the fact that both copper and zinc compounds are of a similar degree of stability. But the composition and color of the deposits will vary with a number of conditions which will require careful control if any desired shade is to be persistently maintained. The percentage of each metal in the deposit will obviously depend somewhat upon their proportion in the solution. Further, an increase in the current density, a reduction in the temperature and a general dilution of the solution make for an increased proportion of zinc.

The solution is worked with a brass anode and at a temperature of 140° F. Additions of free cyanide are required from time to time. Occasional additions of ammonia or ammonium carbonate serve to dissolve up the less soluble basic zinc compounds which tend to separate out, while the presence of a small amount of arsenic, added as arsenious oxide (white arsenic) dissolved in potassium cyanide, serves to brighten the deposit. The presence of sodium bisulphite ($NaHSO_3$), too, inhibits the formation of basic compounds which, floating in the solution, tend to the production of rough deposits by settling on to the cathode.

CHAPTER IX

ELECTRO-DEPOSITION OF METALS—*contd.*

Deposition of Silver.—Many common metals lend themselves much more easily and effectively to coloring processes after they have first received a coating of silver by electro-deposition. Once this is obtained, finishes may be produced which, otherwise, could only be formed on articles of manufactured silver. They may, however, be equally well produced on zinc or zinc alloys, many of which are employed in cheap castings, or on copper, brass and other metals. For effective work, substantially thick deposits must be made, though an eye on cost must always be kept. It must not be overlooked that, in the subsequent process of coloring, the color may have to be removed once or twice before a satisfactorily uniform effect is obtained, and a little silver disappears in each such operation.

As practically the whole of the coloring applied to silver is carried out on work which has been silver-plated, the preliminary deposition of silver is a matter of moment. This is a process which may need to be effected on a variety of metals, including copper, brass, iron and the base metals and alloys, including zinc compositions.

Leaving the detailed treatment of these different metals for a time, it may be well to first indicate the methods of making satisfactory solutions for the electro-deposition of silver.

Silver-plating Solutions.—All practical solutions for this purpose contain, as their essential constituent, the double cyanide of silver and potassium ($AgCN \cdot KCN$). The salt is purchasable and soluble in water. Whether purchased or made by the plater, it is always accompanied by an addition of "free cyanide." This means an excess of potassium cyanide (KCN) over that contained in the silver salt. Its definite purpose will be seen later.

Seldom is this silver compound purchased as such and dissolved in water in order to make a plating solution. The usual practice is to make up the compound from silver nitrate or from silver.

Metallic silver is readily soluble in nitric acid. The metal, as cut strip or grain, is covered with water in a suitable vessel of porcelain and warmed, preferably over a water bath, so that in case of breakage the valuable materials will not be lost. Alternatively a stoneware vessel of suitable size may be floated on hot water. Strong and pure nitric acid is now added a little at a time to bring the metal into solution. Copious brown fumes are given off. These should not be inhaled, and the operation should be conducted in a well-ventilated place. The silver dissolves, giving a clear and almost colorless solution:

$$3Ag + 4HNO_3 = 3AgNO_3 + NO + 2H_2O$$

NO (nitric oxide) is a colorless gas, but, in contact with air, combines with oxygen and forms nitrogen peroxide (NO_2), which is a brown gas. Care and intelligence are required in the operation. Further additions of acid may be required from time to time, but even too much strong acid may be added and the action slow down for the want of water.

Slow evaporation will then yield a mass of crystals of

silver nitrate. From these the remaining liquor can be poured off, further evaporated and thus the whole of the nitrate recovered.

With a little care the yield is practically 100 per cent. Thus :—

Ag forms	$AgNO_3$	
and 108 parts. yield by wt.	$108 + 14 + 48$	
	170 parts by wt.	

Alternatively the silver nitrate may be purchased. A consideration of quantities and costs will doubtless lead to a choice of method to be used.

One ounce of silver per gallon of plating solution will suffice for the purpose now being considered. Solutions for heavy deposits of silver should contain much more metal.

Considering a gallon of solution, 1 oz. troy of fine silver is procured and converted into the nitrate by the method outlined above. Alternatively $\frac{170}{108} = 1{\cdot}58$ ozs. of silver nitrate may be purchased, and the salt is then dissolved in about 1 qt. of distilled water. A Winchester quart bottle is a convenient vessel in which to carry out the operations. Transfer the silver nitrate solution to such a bottle.

Prepare a solution of potassium cyanide containing 4 ozs. av. of 98 per cent white "cyanide" in a quart of water. Ordinary water will suffice for this. Add the cyanide solution to the silver nitrate solution, a little at a time, and shake after each addition. A white precipitate at once forms, and after shaking soon settles, leaving a fairly clear liquid :—

$$AgNO_3 + KCN = AgCN + KNO_3$$

This ppt. is silver cyanide (AgCN). It is insoluble in water. Continue the addition of cyanide with care as long as further precipitate is formed. A point will be reached when a further addition of cyanide will yield no more precipitate, but will begin to clear the solution. The above operation is then completed and the whole of the silver is now in the form of AgCN. The supernatant liquid is now poured off (not thrown away yet). If the operation has been carried out successfully, this liquid will contain no constituent of value, and it may then be thrown away. If the operation has been carried too far, the solution will still contain silver and must be reserved for its recovery.

The precipitate is now washed with water, which is carefully poured away after allowing the precipitate to settle. With care, no loss of silver will be entailed. The precipitate is now pure AgCN. Further additions of cyanide solution are now made with shaking until the AgCN is just redissolved. During this operation :—

$$AgCN + KCN = AgCN{\cdot}KCN$$

Silver cyanide and potassium cyanide combine together and produce a new soluble compound. The equation expresses the fact, and experiment soon confirms that equal quantities of cyanide are required for precipitating and redissolving the silver cyanide.

A further equal amount of " cyanide " solution is now added and the whole solution made up to 1 gal. Use distilled water. Solutions are continually evaporating, and impurities derived from the water are steadily concentrating.

The solution is now ready for use.

The Electrolytic Preparation.—A quite different method of making up the silver solution is as follows:—

Make up a solution of cyanide containing $2\frac{1}{2}$–3 ozs. cyanide per gallon, in a convenient vessel. This can be done without warming. Suspend in the solution one or more porous pots containing a similar cyanide solution, so that the level in the pots is the same, or a little above that in the main vessel. A sheet of fine silver is made the anode (by connecting it to the positive pole of the generator) in the main solution and strips of iron, nickel or silver (preferably silver) made cathode (connected to the negative pole of the generator) in the porous cells. An electric current is passed. Silver dissolves from the anode sheet, and only hydrogen is evolved at the cathode. The weight of silver passing into the solution can be checked by weighing the plate from time to time, and the process stopped when the required ounce per gallon has been attained. It is always an advantage to use an ammeter in the circuit, and a current of 5–10 amperes *per sq. ft. of anode surface* will be found sufficient. A current of 5 amperes will dissolve nearly two-thirds of an ounce of silver in an hour. If too high a current is used the anode sheet will darken considerably, and the speed of solution will be reduced. The anode sheet should slightly darken. This is the electrolytic method.

Working the Solution.—The solution when first made may have a little brown sediment in it. This is not dangerous, nor does it serve any useful purpose. It may readily be removed by filtering through calico, which can be conveniently stretched on a wood frame.

As an anode, fine silver sheet must be used. It should

be annealed before use. In a plating solution, metal should pass into the solution from the anode as rapidly as it is deposited. This is easy from soft anodes. Rolled anodes are ordinarily hard and insoluble, and the required softness is obtained by annealing. This must not be done over a coal or coke fire from which sulphuretted hydrogen (H_2S), which attacks silver, is given off. A charcoal fire or an enclosed muffle must be used, and the comparatively low melting-point of the metal (viz. 950° C.) kept in mind. Standard silver must not be used. This is an alloy containing 92·5 per cent Ag and 7·5 per cent Cu. As an anode, both metals dissolve, and for a long time only silver is deposited. The dissolved copper accumulates in the solution, the silver content diminishing. Sooner or later copper will begin to be deposited. Then the solution will need to be remade.

Pure silver anodes, when in use, slightly darken. A serious darkening and an accumulation of insoluble deposit are due to incorrect conditions. Either the current is too high or the free cyanide content of the solution is too low. The latter is the common cause. Silver dissolves from the anode through the intermediate formation of silver cyanide (insoluble). The purpose of the free cyanide is to keep this dissolved. A lack of free cyanide can easily be made good by limited additions. Where this can be done it is better to keep a check on the free cyanide by the usual silver nitrate test, for which the student must be referred to other books.

It is also preferable to use a rather larger anode than cathode surface. This ensures a smaller C.D. on the anode, and this in turn promotes anode solution, and thus maintains the metal content of the solution.

The silver deposit should be perfectly white and uniformly dead. Grey and dark deposits are due to too high a current. This should not exceed 4–5 amperes per sq. ft. of work. After about five minutes in the solution, the work, when of copper or brass, should be removed, examined and scratch-brushed. This gives an opportunity of examining the adhesion of the deposit. If this is unsatisfactory and stripping is necessary, this will be easier at this stage than when a thicker deposit has been obtained. If the deposit is satisfactory, the work is replaced in the solution and deposition continued for about 30–60 minutes.

Articles of iron, zinc or zinc compositions are usually prepared as for plating, and are then given a thin coating of copper in the cyanide solution. When completely covered with copper they are removed, rinsed, scratch-brushed and lightly scoured and transferred to the silver vat.

A common observation in the silver bath is that articles when first suspended in the solution acquire a white film before the application of the current. This is specially likely to occur when the free cyanide is high. No advantage accrues to this self-whitening—rather the reverse. With, for example, a copper article, a very thin film of copper is passing into the solution and deposits silver in its stead. This silver is thus deposited on a shifting foundation. It therefore cannot be secure, and super-deposited metal will also be insecure. This must be avoided. One method is to ensure that as soon as the work enters the solution current passes on to it before this solution effect can take place. This is the course adopted by many platers.

Another process with the same end in view is that of "quicking."

"**Quicking.**"—By this is meant the deposition of a thin bright film of mercury on the work prior to silver-plating. The film is obtained by passing the work through a suitable solution of mercury, called a quicking solution. By the same process of substitution, a film of the metal dissolves and mercury is thrown down. It behaves very differently from silver in that it amalgamates with the metal and hence adheres very tenaciously. The advantages of this may be briefly stated:—

1. After "quicking" the surface is much less liable to oxidation before the first deposit of silver goes on. The cleaner surface makes for adhesion.

2. Adhesion is further promoted by the amalgamation of the silver deposited.

3. The quicked surface shows no tendency to deposit silver by simple immersion.

The silver which then goes on by electro-deposition is deposited without loss of basis metal. While some platers may dispense with quicking, the use of such solutions as are now to be described is recommended as advantageous.

Quicking Solutions.

"*Acid Quick.*"—Dissolve one ounce of mercury in nitric acid (1 fl. oz. strong acid to 3 fl. ozs. water). The mixture is heated gently on a sand bath. A little more of the acid may be used, if necessary, but a large excess should be avoided. When the mercury is dissolved the solution is diluted with one gallon of distilled water and stirred. Brass and copper, after the usual cleaning processes, receive by merely passing through this solution a bright adherent film of mercury.

"*Cyanide Quick.*"—One ounce of mercury is dissolved in nitric acid as before and diluted to one quart with distilled water. Caustic soda solution (1 oz. NaOH to 10 fl. ozs. water) is now added, and this precipitates the mercury as a yellowish precipitate, which is practically HgO. The precipitate is allowed to settle and the clear liquid poured away, or the mixture may be filtered. The precipitate is now redissolved by adding a solution of potassium cyanide (4 ozs. to 40 fl. ozs. water). This gives a solution of double cyanide of mercury and potassium with an excess of cyanide. The solution, which is accompanied by a dark precipitate in small amount, is now filtered and made up to one gallon. The solution is perfectly reliable in use.

The Quicking Process.—Prior to quicking, all work should be chemically clean, that is, free from grease and oxides. A clean "quick" then results. Unevenness in quicking may be remedied by the use of a potash mop, kept specially for this purpose *and not applied on any other work*. After quicking, the work may with advantage be rinsed with a weak solution of "cyanide" and lightly rubbed with a cotton potash mop. Mercury must not be allowed to accumulate at the bottom of the quicking vessel. If the work touches liquid mercury, much of the latter metal is taken up and this weakens the metal, in addition to inducing a rough deposit subsequently. Such roughness can only be removed by a treatment similar to that of mopping with tripoli compo.

Quicking solutions become weakened with use. It is therefore well to keep a stock or quantity of strong solution from which additions to the working quick may be made as occasion demands.

An imperfect quick may be as fatal as no dipping at all. Unless a good silvery-white coating of mercury is obtained the risk of subsequent stripping is great, if not almost certain.

Deposition of Gold.—Electro-gilding solutions may be made by chemical or electro-chemical methods. Two materials, fine gold and good potassium cyanide, are required. The metal content of the solution is very variable, and so also are many of the conditions of working, and these are soon mastered.

Electrolytic Method.—A solution of 95 per cent grey cyanide is first made containing about $\frac{1}{2}$ lb. per gallon (50 grms. per litre). This is contained in a suitable vessel, and supported in it is a porous pot containing a little of the solution. Into the porous pot is introduced a piece of iron, silver, carbon or other conducting material which, connected to the negative pole of the generator, becomes cathode. The anode—a piece of fine gold—is placed in the main solution, which may preferably be warmed. If a copper connecting wire is used it should not dip into the solution. A current is passed from a 2 to 4 volt circuit, and the gold anode goes into solution. The weight of gold dissolved is registered by the loss in weight of the anode. The process may be continued until the solution contains about 3 dwts. of gold per gallon. Alternatively the condition of the solution may be tested by inserting a clean copper wire, connected to the negative terminal, into the main solution, and it can soon be judged how far the solution meets requirements. As before indicated, a workable metal content is an elastic figure. The porous pot is then withdrawn.

Chemical Methods vary in procedure. A simple method

is to take a good "cyanide" solution, as in the electrolytic method, and add to it the requisite amount of gold chloride. This is an article of commerce, and its metal content may be judged from the fact that a 15-grain tube is usually guaranteed to contain 7 grains of gold. This compound has a formula usually given as $AuCl_3 \cdot HCl \cdot 3H_2O$. Alternatively, the required weight of fine gold may be dissolved in aqua regia (a mixture of nitric and hydrochloric acids). Then :—

$$2Au + 9HCl + 3HNO_3 = 2AuCl_3 + 3NOCl + 6H_2O$$

The acid must be used with discretion, avoiding a large excess. The solution should be evaporated to get rid of excess of acid. Before the liquid attains the consistency of syrup it should be diluted with water and re-evaporated. Complete evaporation to dryness is unnecessary and is to be avoided, as it leads to decomposition.

The gold chloride purchased or prepared is added a little at a time to the cyanide solution, which on warming to 160° F. is ready for deposition. The solution should contain at least 3–4 dwts. of gold per gallon.

This process of dissolving the gold should preferably be done in a vessel of porcelain standing over a vessel containing water which is kept slowly boiling. The arrangement is called a water bath. It may be rigged up in many ways. The liquid in the porcelain vessel is heated by the latent heat of the steam as it condenses to water on the underside of the vessel. The method ensures uniform heating, and avoids undue local temperatures which bring about decomposition of the materials. There is also the element of safety in that, should the vessel containing the gold compound fracture, its contents are not lost. They

may easily be recovered from the water bath. Other methods are available for preparing gilding solutions, but these will now suffice.

Notes on Gilding Solutions.—Solutions for the deposition of gold should contain sufficient free cyanide to keep the anodes clean. A clean crystalline surface on the anode indicates excessive anode solution, due to a large excess of free cyanide. While the gold only goes into the solution—and so is not actually lost—this procedure is undesirable. Large excesses of cyanide are thus to be avoided. Old solutions will sometimes give a slate-grey colour on the anode. More cyanide should not be added to rectify this too soon. Frequently, such dirty anodes will become clean on standing with the current off. When this happens the proportion of free cyanide is not far wrong.

Gilding solutions should be handled with extreme care. Such solutions certainly will clean off grease from the work if it is there, but this is not the function of the gilding solution. Preliminary cleaning should be quite as scrupulous as with other metals. Dirt introduced into the gilding solution must, in fact does, in time impair its working. Again, metallic oxides may easily be removed by the warm gilding solution, but this leads to the formation of metallic compounds in the solution which, in time, will exert an unfavourable influence on the deposit. Zinc is particularly pernicious.

After standing for a time, any dirt which rises to the surface of the gilding solution may be removed by drawing a piece of clean blotting paper over the surface of the solution.

Deposition of Nickel.—This example of deposition

is much more commonly used for protective than coloring purposes. Only a very brief account will be necessary.

The solution used for a long time was :—

Nickel ammonium sulphate .	12 ozs.	75 grms.
Water	1 gall.	1 litre

The solution has a low metal content and the rate of deposition is limited to about 4 amperes per sq. ft. under stationary conditions. More rapid deposition, however, is possible from solutions containing more nickel. A good solution is :—

Double nickel salts .	6–8 ozs.	38–50 grms.
Single nickel salts .	6–8 ,,	38–50 ,,
Ammonium chloride	2–4 ,,	12–25 ,,
Boric acid . .	1 oz.	6 ,,
Water . . .	1 gall.	1 litre

Ammonium chloride is added as a conducting agent and boric acid to prevent the formation of basic salts, which are liable to form at the cathode.

These solutions do not contain any cleansing constituent. Work for nickel plating must therefore be cleaned with scrupulous care, finally passing through a weak solution of cyanide containing :—

Potassium cyanide .	½–1 lb.	50–100 grms.
Water . . .	1 gall.	1 litre

After passing through this "cyanide dip" to remove last traces of tarnish, the work is thoroughly rinsed and immediately transferred to the plating bath, a high C.D. being temporarily used for a first quick coating, afterwards reducing the rate of deposition to 6–8 amperes per sq. ft.

Smooth deposits can only be obtained on smooth surfaces. Severe polishing after deposition is undesirable and not permissible. Prior to plating, the work is polished, freed from grease and lightly scoured with flour pumice or with whiting. After passing through the cyanide dip and rinsing, the work is " struck " in the bath (that is, a quick first coat put on), after which the work should not be removed from the cathode bar or solution until deposition is completed. After rinsing and drying, the final nickel deposit is somewhat dull. The well-known finish is then obtained in the case of heavy deposits by means of tripoli, then white compo and finally lime as a finish and drier. With lighter deposits the tripoli treatment is omitted.

Deposition of Tin.—A large amount of small brasswork is " tinned " by boiling it in a solution made by dissolving about ½ oz. tin proto-chloride (stannous chloride, $SnCl_2$) in one gallon of a saturated solution of cream of tartar (potassium bitartrate, $KHC_4H_4O_6$). The solution is used hot, and the cleaned articles are immersed in it by means of a tin sieve. Alternatively, the articles may be stirred or shaken with grain tin in the hot solution. Subsequently shaking in a barrel with sawdust will effect drying and give the necessary polish. The deposit is, in any case, extremely thin, being produced by what is called simple immersion.

More substantial deposits must be obtained by electro-deposition. A suitable solution is :—

Stannous chloride .	4 ozs.	25 grms.
Ammonium oxalate	10 ,,	62·5 ,,
Oxalic acid . .	½ oz.	3 ,,
Water . . .	1 gall.	1 litre

Dissolve the tin chloride in a limited amount of water, say one-half. Dissolve the ammonium oxalate and oxalic acid in the other half to make a separate solution. Add the oxalate solution to the tin solution a little at a time with stirring. The white precipitate which first forms (stannous oxalate, SnC_2O_4) subsequently redissolves, and the resulting solution, after a short boil, works well with a tin anode.

Only a low-current density is permissible, and the essential conditions will soon be acquired with a little practice.

Electro-deposition of Bronze.—Bronze is the name given to a wide series of alloys consisting of copper with notable quantities of tin. Gun-metal (90Cu·10Sn), bell metal (80Cu·20Sn) and coinage bronze (95Cu·4Sn + 1Zn) are good examples. The presence of a little tin in copper profoundly modifies the properties, mechanical and chemical, and also the colors obtained by chemical processes. Such modification of surface composition may be obtained by the electro-deposition of the alloy. The problem has not been very exhaustively explored, but where applied for metal coloring, uniformity of composition will become of vital importance.

Solution I :—

Tin proto-chloride ($SnCl_2$), 2 lbs., is dissolved in water and treated with caustic soda solution until the precipitate first formed is redissolved :—

$$SnCl_2 + 2NaOH = \underset{\text{white ppt. stannous hydrate}}{Sn(OH)_2} + 2NaCl$$

$$Sn(OH)_2 + 2NaOH = \underset{\text{soluble sodium stannite}}{Na_2SnO_2} + 2H_2O$$

The precipitate may not completely disappear. Sufficient caustic soda has been used when the precipitate reaches an apparently irreducible minimum. This solution is now added to 25 galls. of cyanide copper solution. The mixture is worked with a copper anode, and additions of tin solution will need to be made from time to time. Current from a 6 volt circuit will suffice, and the solution worked at about 120° F.

Solution II :—

Copper sulphate .	2 ozs.	12·5 grms.
Tin proto-chloride .	2 ,,	12·5 ,,
Ammonium oxalate	8 ,,	50 ,,
Oxalic acid . .	½ oz.	3 ,,
Water . . .	1 gall.	1 litre

The copper sulphate and tin chloride are dissolved together in about a quart of water, and the ammonium oxalate dissolved in another quart. The addition of the ammonium oxalate solution to the copper-tin solution produces a mixed precipitate of the oxalates :—

$$CuSO_4 + Am_2C_2O_4 = CuC_2O_4 + Am_2SO_4$$
$$SnCl_2 + Am_2C_2O_4 = SnC_2O_4 + 2AmCl$$

These precipitates could be washed with water. No great disadvantage accompanies the neglect to do this. Further addition of $Am_2C_2O_4$ redissolves these precipitates, giving double oxalates, viz. $CuC_2O_4 \cdot Am_2C_2O_4$ and $SnC_2O_4 \cdot Am_2C_2O_4$. The remainder of the ammonium oxalate and the oxalic acid are essential to good working. The solution is then made up to its correct bulk and worked warm. Of the two metals, the tin is the more difficult of deposition, and an increased current density

therefore tends to a lighter deposit, apart from burning, containing more tin.

Electro-deposition of Cadmium.—The metal cadmium is silvery white and is very readily deposited upon most metals from a cyanide solution, and the deposited metal may well serve as a protection for iron and steel against corrosion and also for decorative purposes. Even under very exposed conditions, cadmium-plated steel tools have remained unaffected over long periods. Many years ago one of the authors mislaid a pair of cadmium-plated scissors in the garden, and, after twelve months' exposure, they were slightly discolored but even less corroded.

Solution :—

Cadmium sulphate . .	$2\frac{1}{2}$ ozs.
Washing soda . . .	q.s.*
Potassium cyanide . .	6 ozs.
Water	1 gal.

The cadmium sulphate is dissolved in about one-half of the total water and the potassium cyanide in the other half. Washing soda solution is added to the cadmium sulphate solution until complete precipitation of the carbonate has been effected :—

$$CdSO_4 + Na_2CO_3 = \underbrace{CdCO_3}_{\substack{\text{cadmium} \\ \text{carbonate}}} + Na_2SO_4$$

The cadmium carbonate is allowed to settle and the clear liquid siphoned off or filtered through calico. A simple filter may be made by stretching a piece of calico across a wood frame. After filtering off, the precipitate is

* q.s. = in sufficient quantity.

washed two or three times with clean water. The washed precipitate is dissolved in the cyanide solution, giving the essential double cyanide of cadmium and potassium $\{Cd(CN)_2 2KCN\}$. The reactions are of the same type as those with zinc in the case of the brassing solution. The solution may be worked cold and still better warmed. An excellent deposit is easily attainable, and copper wire cadmium plated can be drawn down to ·006 in. diameter and still retain a cadmium surface.

In this solution iron goods can be plated direct with cadmium, or copper and cadmium may be used on iron goods to imitate "silver ox." For this purpose the iron is given a stout coating of copper. This is finished up and then given a thin coating of cadmium. The cadmium deposit is then cut through by relieving, thus exposing the copper in parts. Subsequent treatment with ammonium, barium or potassium sulphides will impart a brown to black shade upon the copper, leaving the cadmium practically unaffected. The work is then finished and lacquered.

Deposition of Lead on Iron and Steel.—Several solutions are available for this process, one which, if successfully achieved, should be of immense value for the protection of all metals which are called upon to do service in acid atmospheres.

Solution I :—

Litharge (PbO) . . .	1 oz.
Caustic soda (NaOH) . .	6 ozs.
Water	1 gal.

The caustic soda is dissolved in a quart of water and the lead oxide added with warming. There will be a

slight residue. The solution is made up to 1 gal. with boiled or distilled water, allowed to stand for a few hours and then decanted from the residue. For the deposition, a lead anode is used and the iron and steel work cleaned in the usual manner. It is well to ensure a first quick coating of lead, and then to cut down the current to obtain only a slow and smooth deposit. Excessive current produces a loose crystalline and useless deposit. Brass battery terminals may be advantageously treated in a similar manner.

Solution II :—

Lead Cyanide Solution.—For 1 gal. dissolve 5 ozs. lead acetate in 1 pint of distilled water. To the solution add sufficient sodium cyanide or potassium cyanide solution to precipitate the lead as cyanide (similar to making silver-plating solution). Avoid excess of cyanide. Allow precipitate to settle, decant off clear liquid and redissolve the precipitate in a strong solution of cyanide. Subsequently make up the bulk of the solution to 1 gal. The solution may be used for any metals ordinarily plated in cyanide solutions. Clean copper may even receive a coating by simple immersion. When a coating of lead has been obtained, it is scratch-brushed, using as lubricant, water containing 4 fl. ozs. vinegar and 1 dr. of gelatine (or best glue, such as is used in bob-dressing) per gallon.

The process of deposition is easy, but only a low current density can be used. It must be remembered that lead gives a much heavier deposit for the same current than copper, and it also has a lesser tendency to form a compact deposit. Hence slow deposition must be the rule.

The Lead Perchlorate Solution gives the best lead deposit of all the solutions in common use. Its composition is as follows :—

Lead (as perchlorate) .	50 grms.
Free perchloric acid .	20–50 ,,
Peptone . . .	·5 grm.
Water . . .	1 litre.

The method of making up this solution is a little beyond the scope of this book, and some chemical knowledge is required for it. It may, however, be briefly indicated. Perchloric acid ($HClO_4$) is, as a solution in water, an article of commerce. Its strength is first found, and from this, definite amounts of the real acid can easily be measured off. Two amounts are taken, the first, sufficient to dissolve the lead as lead oxide :—

$$\frac{PbO}{Pb} = \frac{223}{207} \therefore 50 \text{ grms. Pb} = \frac{50 \times 223}{207} = 54 \text{ grms. PbO.}$$

The oxide dissolves easily and the free acid is then added. Peptone constitutes the addition agent, and is dissolved in a few ccs. of water and added to the bath. The solution will be found to be the most costly of the lead-plating baths, but the results obtained from it may well be considered to outweigh the cost.

The solution is used cold with, of course, a lead anode. A comparatively high-current density of 18–27 amperes per sq. ft. is possible, so that thick deposits are readily produced. Portions of the cathode which are unduly exposed to the anode are apt to be a bit rough, owing to unequal distribution of the current.

Lead Acetate Solution.—A solution made up as follows :—

Lead acetate . . .	1 lb.	100 grms.
Ammonium perchlorate .	6 ozs.	40 ,,
Acetic acid . . .	3 fl. ozs.	20 c.c.
Water	1 gal.	1 litre

yields a good deposit when aloes extract is used as an addition agent.* Details should be referred to in the reference given. Periodical additions of the addition agent are necessary, but the current density cannot exceed 10 amperes per sq. ft. The solution is cheaper than the perchlorate bath, but is certainly not so good.

* "Trans. Amer. Electrochem. Soc.," Vol. XXIV, p. 315, 1913.

CHAPTER X

COLORING OF COPPER

Properties of Copper.—While copper is tolerably stable in dry air, moist air containing traces of acid, and, of course, carbonic acid gas, brings about rapid tarnishing, and thin films, varying from reddish brown to black, appear in course of time. Some idea of the effect of the state of the atmosphere may be gathered from the behaviour of unlacquered domestic polished copper on (1) dry and (2) moist and foggy days. The rapid effects obtained in a damp atmosphere increase with time, and the copper, in addition to the general darkening, may acquire green deposits of a basic carbonate of copper, which is frequently but incorrectly described as verdigris.

In the air, moisture, oxygen, carbon dioxide, acids and sulphuretted hydrogen each add their quota to the general effect, and the deposits obtained may consist of red cuprous oxide (Cu_2O), black cupric oxide (CuO), cuprous sulphide (Cu_2S) and hydrated carbonates of copper.

Oxides of Copper.—Combination of copper and oxygen is accelerated by heat. A piece of clean copper held in a clear (Bunsen) flame acquires a red deposit (Cu_2O) some distance from the flame and a black deposit (CuO) at the points of greatest heating. Between these two extremes many intermediate mixtures and shades of the oxides may be obtained. This natural coloring of

copper may be, and very frequently is, very uneven. One of the objects of metal coloring is to secure, with rapidity, uniform films of these oxides of suitable shade and permanence. The oxidation of the copper may be carried out to so great a degree that the whole of the metal may be converted to oxide. In fact, large quantities of the two oxides of copper occur in nature and constitute a source from which much marketable copper is obtained. It may, in passing, be of interest to mention that, according to the generally accepted view, the earth was, in its initial stages of formation, gaseous, and then molten and at a very high temperature. No chemical compounds then existed. Their formation only became possible as the temperature fell, and then combination of the elements began in a definite order, an order which can with some accuracy be computed from our knowledge of the stability of existing compounds. Chemically active metals like sodium, potassium, aluminium, magnesium and zinc were entirely converted into compounds. These metals are never found free in nature. Such metals as copper, silver, gold, mercury and platinum are slow in chemical combination, and these in greater or lesser quantities survived the processes of combination and are therefore sometimes found in the free metallic form.

Carbonates of Copper.—A green compound frequently called copper carbonate and written $CuCO_3$ is an article of commerce. It may be obtained by adding sodium carbonate solution to a solution of a copper salt. The following change might be expected :—

$$CuSO_4 + Na_2CO_3 = CuCO_3 + Na_2SO_4$$
green ppt.

When this mixture is made, careful observation shows that a gas is simultaneously evolved. This is carbonic acid gas, and is not accounted for in the above equation. It is due to the fact that the $CuCO_3$ probably formed originally, is unstable and is decomposed by water when:—

$$CuCO_3 + H_2O = Cu(OH)_2 + CO_2$$

Copper hydroxide, $Cu(OH)_2$, is a well-known and definite compound, but the green precipitate obtained with Na_2CO_3 is not entirely $Cu(OH)_2$. It appears to be a compound of copper carbonate and copper hydroxide. Two such double compounds occur in nature, and from them marketable copper is obtained. They are:—

1. Malachite (green) $CuCO_3 \cdot Cu(OH)_2$
2. Azurite (blue) $2CuCO_3 \cdot Cu(OH)_2$

These, again, have been formed by long and slow natural processes, and some very fine examples are to be seen in many of our museums. Thus while we may frequently refer to a substance as copper carbonate, the term will be understood to cover also these hydrated carbonates, or "basic" carbonates as they are called. For many, in fact most, chemical purposes, they all act in the same manner, and might almost be used interchangeably. These deposits are found on copper which has long been buried in moist earth, and the external green deposit frequently covers a lower deposit of cuprous oxide (yellow or red) to which carbonic acid gas has not had easy access. The films—or patinas as they are called—give very pleasing effects, and attempts are made to imitate them in the various methods of "antique" bronzing.

Acetates of Copper.—Copper acetate, $Cu(C_2H_3O_2)_2 \cdot H_2O$,

is a green salt, a solution of which is obtained by dissolving the oxide, hydroxide or carbonate in acetic acid, e.g.

$$Cu(OH)_2 + 2H{\cdot}C_2H_3O_2 = Cu(C_2H_3O_2)_2 + 2H_2O$$

The solid may then be obtained by crystallisation. When, however, copper is exposed to the action of acetic acid fumes and air, a basic acetate is formed. This is the compound known as verdigris,

$$6Cu + 8H{\cdot}C_2H_3O_2 + 3O_2 = 2\{Cu(OH)_2{\cdot}2Cu(C_2H_3O_2)_2\} + 2H_2O$$

verdigris

and this compound results from the treatment of copper articles with acetic acid, copper acetate or other acetates. It is poisonous but insoluble in water, and is converted into the normal acetate by dissolving in dilute acetic acid.

Sulphides of Copper.—There are two sulphides of copper :—

Cuprous sulphide, Cu_2S, and
Cupric sulphide, CuS.

Practically the whole of the coloring done on copper with sulphide solutions produces cuprous sulphide, which thus plays a conspicuous part in metal coloring. It is produced in many shades from reddish brown to deep black, the shade depending upon a number of factors, that of thickness of the film being probably the most important. Metal coloring is beset with so many conditions that it is wellnigh impossible to predict the exact shade which will be produced from a given set of conditions except by trial. Only a general indication can be given based on the known colors of the compound constituting the color. Speaking generally the

sulphide of copper may result from one or other of the following reactions :—

$$2Cu + H_2S = Cu_2S + H_2$$
$$2Cu + K_2S + 2H_2O = Cu_2S + 2KOH + H_2$$

The ease with which copper combines with sulphur when the two elements come into contact is reflected in the large quantities of Cu_2S which occur in nature. By far the larger proportion of the copper which comes on to the market is obtained from this naturally occurring compound. The combination of the two elements is interestingly shown by a heated copper wire which, introduced into the vapour of sulphur, burns with rapidity forming the sulphide :—

$$2Cu + S = Cu_2S$$

Copper Sulphate.—This is a very well-known salt of copper. It is otherwise called blue vitriol and bluestone. The crystallised salt is $CuSO_4 \cdot 5H_2O$, the water being definitely but loosely combined. At 100° C. the crystal loses four-fifths of its water and becomes a bluish-white powder, $CuSO_4 \cdot H_2O$, while at 260° C. it then becomes $CuSO_4$, which is white dehydrated copper sulphate. This white compound is deliquescent, and in contact with water re-forms the blue salt with the evolution of considerable heat. At a still higher temperature $CuSO_4$ decomposes thus :—

$$CuSO_4 = CuO + SO_3$$

In contact with copper it forms at an elevated temperature cuprous sulphate, Cu_2SO_4, which on heating leaves cuprous oxide of varying shades from red to brown :—

$$Cu_2SO_4 = Cu_2O + SO_3$$

Copper sulphate is an important coloring agent, and the foregoing reactions indicate the course of the changes which it may undergo with copper or brass.

Copper Nitrate.—The blue crystallised compound is $Cu(NO_3)_2 \cdot 3H_2O$. When heated it loses nitric acid and changes to a basic nitrate :—

$$4Cu(NO_3)_2 \cdot 3H_2O = Cu(NO_3)_2 \cdot 3Cu(OH)_2 + 6HNO_3 + 6H_2O$$

At a high temperature it is further decomposed to oxide :—

$$Cu(NO_3)_2 \cdot 3Cu(OH)_2 = 4CuO + 2HNO_3 + 2H_2O$$

In its chemical reactions it must be regarded as an oxidising agent, which accounts for the colored films of oxides obtained on copper and brass by its means.

Chlorides of Copper.—There are two chief chlorides of copper :—

1. Cuprous chloride, Cu_2Cl_2—a white insoluble (in water) substance which, however, is soluble in hydrochloric acid, forming a brown solution, and in ammonia forming a blue solution.

2. Cupric chloride, $CuCl_2 \cdot 2H_2O$, a green soluble salt. By heating, this first loses its water and then is further decomposed as follows :—

$$2CuCl_2 = Cu_2Cl_2 + Cl_2$$

The reaction is very important in the chemical industry. The compounds are of interest here in connection with the deposits obtained by the action of chlorides on copper, and by the long exposure of copper to sea water. These saline products are usually yellowish green basic chlorides of copper. One of green deposits has the formula $3Cu(OH)_2 \cdot CuCl_2 \cdot H_2O$. A similar substance occurs in

nature and is known as atacamite. Under the green deposits produced by sea water there may be found a film of a decidedly yellowish red compound. This is hydrated cuprous oxide (Cu_2OH_2O).

Reference may also be made to the existence of actinic properties in some of the chloride of copper compounds. This is discussed on page 148. The actinic compound appears to be a subchloride of copper, and the effect of light and air is possibly to convert this to

$$3CuO{\cdot}CuCl_2{\cdot}4H_2O$$

which is dark green in color.

Ammoniacal Compounds of Copper.—When ammonia is added to copper sulphate solution a green precipitate is first formed. This is a basic sulphate which is largely composed of hydroxide. It readily dissolves an excess of ammonia to a deep blue solution, from which deep blue crystals can be obtained which have the composition $CuSO_4{\cdot}4NH_3{\cdot}H_2O$. Similarly, dry copper sulphate combines with NH_3 and evolving heat (cf. water) produces $CuSO_4{\cdot}5NH_3$. This compound, on heating, first loses NH_3 and becomes $CuSO_4{\cdot}NH_3$. These reactions are very similar to those with water, but these ammoniacal compounds play a large part in some coloring processes.

Similar deep blue compounds are formed when copper oxide, hydroxide, nitrate or chlorides are treated with ammonia. Thus black copper oxide readily dissolves in ammonia and this provides a method of cleaning copper and brass. It impresses the lesson, too, that where ammoniacal solutions are being used for the production of colored films of oxides, an excess of ammonia will be

fatal to the production of the color. Hence the recommendation which will be found, to avoid excess by leaving some of the basic precipitate undissolved.

Precipitation of Metal Films on Copper.—Reference must now be made to the action of copper on many metallic solutions and the application of these reactions in metal coloring. Solutions of mercury, silver, arsenic, antimony and other metallic compounds are decomposed by copper, the deposited metals forming more or less adherent films on the surface of the copper. With a mercury salt :—

$$HgCl_2 + Cu = CuCl_2 + Hg$$

the mercury being deposited as a bright film if the process is slow. This principle is applied in " quicking " prior to silverplating. With a silver salt :—

$$2AgNO_3 + Cu = Cu(NO_3)_2 + 2Ag$$

The silver is usually a grey loose deposit of no " silvering " value. With an arsenic compound :—

$$2AsCl_3 + 3Cu = 3CuCl_2 + 2As$$

very satisfactory steel grey deposits of arsenic are obtained. Doubtless the first film of arsenic alloys with the copper, and an alloy containing 32 per cent of arsenic and 68 per cent of copper is formed.

In all these cases a quantity of copper passes into solution. Such a disintegrating surface is not usually ideal for receiving adherent films of metal. The case of mercury is, of course, exceptional, while in the case of arsenic the difficulty would be lessened if alloying of the two metals takes place.

General Remarks on Coloring of Copper.—One obser-

vation which will soon be made in the coloring of copper is the effect of the composition of the metal on the color produced. Even slight amounts of impurities effect marked differences on the colors. Speaking generally, the colors are darkened with impure metal, while the best tones will be obtained on deposited copper, which is notoriously pure. Frequently, therefore, the recommendation is made that even in the case of articles manufactured in copper, copper deposition should still be resorted to.

CHAPTER XI

COLORING OF COPPER (*cont.*)

Black Copper "Ox"—China Finish—Gunmetal Finish.—This very popular and useful shade is readily produced, but the materials, both metal and coloring agent, must be in good condition. The metal must be thoroughly clean and the potassium sulphide of good quality and in the correct solution strength. Potassium sulphide is decomposed on exposure to air, due to acid fumes and even carbonic acid. With acid fumes :—

$$K_2S + H_2SO_4 = H_2S + K_2SO_4$$

sulphuretted hydrogen is readily evolved, and with it the coloring power of the material disappears.

Solution :—

Potassium sulphide (liver of sulphur)	2 ozs.	12½ grms.
Ammonium chloride	2 lbs.	200 ,,
Water . . .	1 gal.	1 litre

The solution is used cold. It may be used warm, but should then be diluted to one-half strength. The liver of sulphur may be used in the absence of ammonium chloride, but a less satisfactory shade is obtained. The solution may be applied either by immersing the article or by means of a brush. Rinsing in cold, then in hot water and drying in sawdust completes the operations.

The color produced is a sulphide of copper, probably cuprous sulphide (Cu_2S) :—

$$K_2S + 2Cu + 2H_2O = Cu_2S + 2KOH + H_2$$

It may vary from light brown to nearly black. If produced quickly, as in a stronger solution, it is apt to be non-adherent. Slow production in dilute solutions is preferable. The dark shade is usually first produced. From the higher parts it can be wholly or partially removed or relieved by mopping dry or by gentle rubbing with fine damp pumice powder applied with a piece of felt, soft rag or even with the finger. The dark shade is thus toned down to shades distinctly lighter, and very pleasing effects can thus be obtained. If the rubbing has been too heavy and the contrast of color too marked, a momentary application of some of the weakened solution will alleviate the contrast. After drying, the work is wiped with a soft cloth, or lightly brushed or mopped and lacquered.

This shade may be produced on other metals. For this purpose brass should be heavily coppered and iron needs similar treatment, but in this case in the cyanide solution. Ordinary copper may be improved for receiving this finish by being first coppered in the acid bath. Precautions to avoid spotting out (see page 79) should be taken.

Brown Copper "Ox" Solution.

Barium sulphide (BaS)	2 ozs.	12½ grms.
Water . . .	1 gal.	1 litre

With this, or even a more dilute solution, the procedure followed is that given above for the black "ox." The solution may be used cold or warm. It is quicker when

warm, but under more control when cold. The shade produced should be a little darker than that actually required for the finish. After rinsing the methods of relieving given above may be applied. The whole operation is very elastic, and gives wide scope for artistic effect by the variation of solution strength and temperatures and treatment of relieving.

Florentine Bronze.—There are two well-known methods of producing this beautiful color on copper, the one dry and the other wet.

1. *Dry Method :—*

Red oxide of iron . .	2 parts by weight
Black lead . . .	1 part by weight

These are mixed to a paste with either water or methylated spirit, and painted on to the article to be colored, which is now dried off at a temperature of 100° F. for about half an hour. When cooled the loose powder is removed with a stiff bristle brush, when the copper will be found to be colored. This effect is due to the oxidation of the copper at the expense of the oxide of iron, thus :—

$$2Cu + Fe_2O_3 = Cu_2O + 2FeO$$

Darker shades are produced with a higher temperature. An unsatisfactory color can be entirely removed and the process repeated. A better shade will be obtained if the article is first coppered in the acid bath (iron, zinc, etc., passing through the copper cyanide solution first). Even a copper article may be advantageously coppered before coloring. When a satisfactory shade has been obtained it is rubbed with a little methylated spirit and a soft brush till dry, and finished by brushing with

a beeswax mixture containing beeswax dissolved in warm turpentine, to which a few drops of olive oil are added.

2. *Wet Method.*

Solution :—

Barium sulphide . .	1½ ozs.	10 grms.
Water	1 gal.	1 litre

The properly cleaned article is immersed in this solution at a temperature of 120° F. Coloring soon commences and is allowed to proceed until a dark brown, approaching black, has been attained. It is then rinsed in cold and hot waters, dried out in hot sawdust and finished on a dry scratch brush slightly lubricated with a mixture of blacklead and methylated spirit. If the color is too dark it may be reduced somewhat by dry scratch-brushing with a soft wire scratch brush until the right shade is attained, and then either waxed or lacquered with a copper-tinted lacquer.

Barbedienne Bronze on Copper.—This is an excellent effect when well done, and amply repays the trouble in producing it. This is a case in which copper containing a little tin as an impurity gives a better effect than pure copper.

Solution I :—

Antimony sulphide . .	2 ozs.	12½ grms.
Caustic soda . . .	8 ,,	50 ,,
Water	1 gal.	1 litre

The solution is used at 120° F. The article, cleaned as usual, is then scratch-brushed with wet pumice powder and immersed in the solution for 12–16 seconds, afterwards rinsing cold and hot and drying in sawdust and dry scratch-brushing. The article is now passed through

a similar solution of half strength and used cold for a few seconds and finished off, relieving the high lights. The work is then lacquered, drying at 75° F. for about 20 minutes. An opaque or egg-shell finish is now imparted by applying the beeswax mixture.

A darker tone may be produced if, after passing through the first solution, the work is given a 5 seconds' immersion in a copper sulphate solution containing one part by weight of the salt to twenty of water prior to finishing.

Solution II :—

Potassium sulphide .	2 ozs.	12½ grms.
Water	1 gal.	1 litre

Pass the cleaned metal through this solution and, after rinsing, tone in

Sulphuric acid or hydrochloric acid . .	1 oz.	6 grms.
Water	1 gal.	1 litre

after which the usual rinsing and finishing processes are applied as indicated in the case of the previous solution.

Nut Brown on Copper.—This pleasing tone is obtained by passing the cleaned work through a cold solution of ammonium sulphide, the strength of which may be varied between wide limits. Only a momentary dip is required, followed by rinsing and drying out. The tone may now be varied to taste by dry scratch-brushing.

Another effect may be produced by first passing the work through an ammonium sulphide solution of varying strength. A fine velvety surface is produced, the depth of the shade varying with the strength of the solution. This deposit easily rubs off, but may be fixed by passing the article after coloring through methylated spirit.

It is then ignited and finished by the application of a quick-flowing lacquer.

Statuary Bronze.—Very fine rich brown shades suitable for statue bronzing may be obtained from the following

Solution :—

Potassium sulphide .	1¼ ozs.	2 grms.
Ammonium sulphate .	¼ oz.	·4 grm.
Water	5 gals.	1 litre

The solution is used cold. The preparation of the work needs some care, and both bright and dead surfaces may be effectively required on the same piece of work. The treatment for this will now be quite familiar. The prepared work is passed through the solution for a few seconds until a variegated shade is obtained. It is then rinsed and dried off in hot sawdust, and the shade developed by dry scratch-brushing. The work is then either wax-finished or lacquered.

Auburn Brown.

Solution :—

Copper sulphate . .	4 ozs.	25 grms.
Ferric oxide . . .	5 ,,	32 ,,
Water	1 gal.	1 litre

The copper sulphate is dissolved in the hot water, and sufficient caustic soda added to produce the green precipitate of hydroxide. Ferric oxide is now added to the muddy mixture and the whole well stirred. The work is passed through the mixture, removed and heated on a hot plate, the immersion and heating being repeated until a reddish brown color with a violet shade is obtained. A good light is necessary to observe the violet shade. The work is then finished by dry scratch-brushing and lacquering with a transparent or copper-tinted lacquer.

Antwerp Green.—This effect is specially suitable for undercut figures.

Solution :—

Hydrochloric acid . .	1 quart	330 c.c.
Copper acetate . .	3 lbs.	400 grms.
Copper carbonate . .	1 lb.	130 ,,
Arsenious acid . .	½ ,,	65 ,,
Ammonium chloride .	3 lbs.	400 ,,
Water	3 quarts	1 litre

These materials are well mixed and boiled for 20 minutes, after which they are allowed to stand for 12 hours. The solution is then applied to the work with a brush, being well worked into the undercut parts and evenly distributed over the high lights. The work is set aside to dry, any tendency to unevenness being rectified. It is then gently warmed and dusted with a soft brush to remove loose coloring material. A soft paste of a mixture of beeswax and turpentine is then worked in all over the surface with a soft brush, and the work again heated in the oven for 10 minutes. A soft brushing then serves to remove any unevenness in the wax. Rubbing with a pad of soft leather is then applied to shade off from the low to the high lights on the highest portions of which the copper may be nearly exposed, giving a copper-green sheen. A final polish with soft velvet or a fine hair polishing brush completes the treatment.

Copper Medal Bronze.

Solution :—

Copper sulphate . .	4 ozs.	25 grms.
Caustic soda . . .	q.s.	q.s.
Red oxide of iron . .	4 ozs.	25 grms.
Water	1 gal.	1 litre

Dissolve the bluestone in the water and add the caustic soda, producing a green precipitate of copper hydrate. The oxide of iron is then added and the mixture boiled for 10 minutes. The mixture is now cooled down to 160° F. and the work passed through. In the case of large work, this should be raised to 180° F. and the solution brushed over. In either case the work is then heated on a copper sheet on a hot plate until a red-brown shade is produced. When cool enough to handle, brush with a medium bristle brush lubricated with beeswax. Another few minutes on the hot plate is followed, when the article is cold, by a final polish. An unsatisfactory color can always be removed by dry scratch-brushing and the process repeated.

Patina Green on Copper.

Mixture :—

Calcium chloride . .	5 ozs.	32 grms.
Copper nitrate . .	5 ,,	32 ,,
Ammonium chloride .	5 ,,	32 ,,
Water	1 gal.	1 litre

The mixture is prepared as finely as possible by grinding in a mortar.

All work for this process requires copper-plating. This remark even applies for copper articles. Other classes of work should be heavily coppered—zinc, iron, etc., in the cyanide solution. The prepared work, scratch-brushed after plating, is now treated with the above mixture by evenly applying with a brush, special attention being paid to the crevices. The work is then allowed to dry, a yellowish green color resulting. It is warmed and waxed, allowed to cool, and again briskly brushed with a brush moistened with turpentine and

rubbed on a lump of beeswax. The effect is improved by the relief of the high lights.

Black Steel.

Solution :—

Arsenious oxide . .	20 ozs.	125 grms.
Hydrochloric acid . .	1 gal.	1 litre
Copper sulphate . .	10 ozs.	62 grms.
Ammonium chloride .	2 ,,	12·5 ,,

Dissolve the arsenious oxide in the warmed hydrochloric acid and then add the remaining compounds. Stir to obtain complete solution and allow to stand for one day.

All work, other than copper, is first somewhat heavily copper-plated, finishing in all cases in the acid bath, the copper deposit from which gives an excellent result. The coloring solution is used either cold or warm. For a quick effect the solution is heated to 120° F. and the work passed through. An unsatisfactory result may be removed and another attempt made. If a second attempt fails it may be advisable to put on a further deposit of copper. No other metal should be exposed to the solution. The correct color is similar to that of steel which has been fired or annealed.

Alternatively, the work may be made the cathode in the solution, using a carbon anode and a P.D. of about 3 volts.

In either case the work is rinsed through cold and hot waters, and after drying out is toned down on a dry scratch brush. Relieving, if required, can now be effected, a bright relief with a felt bob or cotton mop, using tallow and lime, or a dead relief with wet sand or pumice applied with a piece of cork. Excess of relieving material is then removed, and after drying, a final polish is given with a soft leather or cloth and the work lacquered.

Electro-bronze Shades.—Several shades of a permanent nature may be obtained from the following :—

Solutions :—

A	Nickel ammonium sulphate	2 ozs.
	Water	1 qt.
B	Arsenious oxide	½ oz.
	Potassium cyanide	½ lb.
	Water	2 qts.
C	Sodium thiosulphate	2 ozs.
	Water	2 qts.
D	Caustic soda	4 ozs.
	Water	1 qt.
E	Ammonium carbonate	2 ozs.
	Water	1 pint

Solution D is added to A, followed by solution E with stirring. Then add solution B, again stirring with each small addition. Finally, solution C is added and the whole heated up to 160° F. for 10 minutes, with stirring. The surface is then sprinkled with powdered sulphur and the whole cooled.

The mixture is now used as a plating bath, with anodes of iron, nickel or copper, and a wide range of current density obtained from a terminal pressure of 2–8 volts. All metals, with the exception of aluminium, may be treated in this solution, and the temperature varied up to 185° F. The following results may be obtained :—

On phosphor bronze and copper	black steel and variegated shades
On silverplated copper	pale straw to orange and blue
On brass	crimson-blue, golden yellow and slate-blue.

Variations of temperature, current density and motion of the work all contribute to shade variations. The crimson shade is difficult to obtain, as it rapidly changes to a further shade. Occasional additions of cyanide are necessary. If the results are patchy, scratch-brushing may be resorted to and the work returned to the bath. When a satisfactory shade has been obtained the work is rinsed and dried out, polished with a soft cloth damped with olive oil, followed by a soft dry cloth and lacquered with a transparent lacquer, hardening in a stove for half an hour at a temperature of 100° F.

Imitation Silver "Ox."—For a cheap class of work a good imitation silver " ox " may be obtained on copper by " stopping off " the relief parts and then plating with nickel. The stopping-off varnish is then removed by means of turpentine and, after due cleaning, the work is passed through the following

Solution :—

Potassium sulphide . .	1 oz.	6 grms.
Ammonium chloride .	2 ozs.	12 ,,
Water	1 gal.	1 litre

After coloring, rinse, dry out, rub with a soft cloth free from dust and lacquer.

Brass work is treated by first giving it a good stout coating of nickel. It is then scoured with pumice and copper-plated in the acid bath. After rinsing and drying the copper is polished through to expose the nickel on the high lights. Treatment in the above solution then follows, finally drying and lacquering.

The treatment of iron is the same as for brass, except

for an original coat of copper first from the cyanide bath, and then the acid bath.

Rouge-Brown to Black.—The copper work is first suitably prepared, either bright or matt, and freed from grease with potash. Bright work is then scoured with a wet mixture of whiting 2 parts and Sheffield lime powder 1 part, rinsed through a cyanide dip and immersed in the following

Solution :—

Copper chloride . .	2½ lbs.	250 grms.
Water	1 gal.	1 litre

The solution is kept nearly boiling, and a few minutes suffices to obtain a rich rouge-brown colour. A still richer colour is obtained if the work is first coppered in the acid bath. This color, as explained on page 134, is darkened by exposure to natural light to a bluish shade while the color is unaffected by artificial light. A parcel effect may thus be obtained by first producing a brown (see page 138) on the article of copper and finishing by rinsing, drying and dry scratch-brushing. The hot copper chloride solution is then applied by a neat pad to those parts required in the darker shade and allowed to dry in good daylight. A neat application of the solution will be necessary to obtain a good effect. Finish by dry scratch-brushing and lacquering. Ordinary cast copper in the copper chloride solution assumes a chestnut shade of brown which also subsequently darkens by exposure to natural light.

Terra-cotta Brown.—This is another color which is best obtained on pure copper, and for which purpose

therefore work should preferably receive a stout coat of copper in the acid bath.

Coloring Solution :—

Copper acetate . .	4 ozs.	25 grms.
Copper sulphate . .	3 ,,	19 ,,
Water	1 gal.	1 litre

The solution is used at 180° F. and the prepared work is passed through. The first effects may be patchy, when the color may be removed by scratch-brushing and the work re-immersed. When the shade is satisfactory the work is finished by rinsing, drying out, dry scratch-brushing and lacquering.

Various Brown Shades may be obtained on copper by immersion in a hot solution of copper sulphate.

Solution :—

Copper sulphate . .	5 lbs.	500 grms.
Water	1 gal.	1 litre

This solution, at a temperature of 120° F., gives a light brown shade on pure copper, but with ordinary copper the shade is decidedly darker. If the copper contains appreciable quantities of metals such as zinc or tin the color may be dark brown or even black (see page 136). The uniform conditions required for uniform results are not always obtained at once, and scratch-brushing and re-immersion several times may be necessary before a satisfactory result may be obtained. After rinsing and drying the work is dry scratch-brushed and lacquered.

Red Copper.—A shade of red differing from that of copper may be obtained upon this metal by the following method.

Solution :—

Copper sulphate . .	4 ozs.	25 grms.
Sodium chloride . .	2 lbs.	200 ,,
Water	1 gal.	1 litre

The solution is used 120° F. and the cleaned metal immersed for a short time, afterwards rinsing in hot water and drying off in sawdust. It is then lacquered with transparent lacquer. Experience shows that darker colors are obtained when impurities occur in the copper.

Purple Copper is produced by similar treatment in a

Solution of :—

Sodium hyposulphite .	8 ozs.	50 grms.
Nitric acid . . .	$\frac{1}{2}$ fl. oz.	3 c.c.
Water	1 gal.	1 litre

Royal Copper.—This is a red color obtained by producing a thin film of cuprous oxide (Cu_2O) on the surface by means of heat. It is then polished with soft calico or felt and a paste of rouge powder and methylated spirit. An excellent enamel lustre surface is obtained.

Alternatively, immerse the article of copper or heavily plated copper in fused potassium nitrate contained in an iron pot. The work should, of course, first be dried. A coating of black oxide is formed. Remove, cool and immerse in paraffin oil. Dry out in sawdust. Polish as before. The black oxide is thus removed and the red oxide film is then exposed. Medals and medallions colored in this manner assume a beautiful appearance. The effect is improved by a preliminary coating of lead.

Blue Color on Copper.—(Bancroft's blue)—An exceptional example of a good blue color on copper was

first shown by Bancroft in 1912.* His method is as follows:—

Solution :—

Copper acetate	10 grms.
Gelatine	3 „
Water	1 litre

Cleaned and burnished sheets of copper served as anode and cathode, and a current of from ·15–·45 amperes per sq. decimetre (1·4–4·2 amperes per sq. ft.) was passed for five minutes. The solution was at room temperature. No gas evolution occurred, but the cathode became covered with a thin pale brown deposit which had a slippery surface due to the deposition of gelatine with the copper. Unintentionally one of these deposits was allowed to stand for some time in the solution from which it had been produced, when, without the passage of further current, the plate assumed a purplish blue of extraordinary brilliance and beauty.

The subject was therefore closely investigated. A second electrode was prepared with a deposit of gelatine copper, and after rinsing in cold water was immersed in a 5 per cent copper acetate, not, however, containing gelatine. A remarkable series of color changes occurred upon the surface of the copper deposit. Hues of startling evenness and intensity followed each other in regular succession until the plate had acquired a magnificent deep blue coloration. This process Bancroft called "development," on account of its striking resemblance to the process of development in photography.

Further work showed that gelatine is essential in the

* "Trans. Amer. Electrochem. Soc.," XXII, p. 287, 1912.

depositing process, but not in the development. In the deposition the best content of gelatine is from ·25–·66 per cent, while the best temperature did not exceed 40° C.

Apparently the most satisfactory explanation of the process is that the blue color is due to the absorption on the surface of the gelatine film (such superficial absorption is usually called adsorption) of hydrous copper oxide, a soluble form of copper hydrate which is due to the hydrolysis (decomposition by water) of copper acetate.

This blue color—Bancroft's blue—can then be rendered more stable by lacquering.

CHAPTER XII

COLORING OF BRASS

Brass.—Brass is the name given to a wide range of alloys composed of copper and zinc. In a very restricted sense the term denotes an alloy of copper and zinc in the approximate proportions of 2 : 1. The wider sense must here be understood, and the content of copper may vary from 90 down to 50 per cent or even less. If a third essential constituent is present some suitable modification of the name can at once be made, and the alloys long called German silvers, which, however, do not contain silver at all, may thus be called nickel brass. Brass containing much copper is red in color and is very malleable. With increasing zinc the color becomes paler and is nearly white when the zinc percentage is from 50–60. The increasing zinc makes the brass harder and less easily workable. Brasses with 70 per cent of copper and over are workable cold, while with from 50–70 per cent copper working—such as rolling—is effected hot.

A few typical alloys of zinc and copper may be tabulated :—

Name.	Percentages of	
	Copper.	Zinc.
Bronze powder . . .	82–99	18–1
Tombac	80–98	20–2
Cartridge brass . . .	70	30
Ordinary brass . . .	66	34
Yellow brass	61–65	39–35
Cast brass	62	38
White brass	44	56
Brazing solder	50	50

Further, two samples of gilding metal are as follows :—

	Cu.	Zn.	Pb.	Sn.
1	64	32	3	1
2	78	18	1	3

It is therefore extremely probable that the metal colore will meet a number of these different compositions, anc this without any other knowledge of their compositior than that which is to be gained by the observation of th color or the nature of the article in which the bras appears.

Chemical Properties of Brass.—Now the properties o an alloy are not to be altogether guessed from those of it constituents. Very profound changes of properties occu in a metal by the addition of even only a very smal proportion of a second constituent. There is certainly room for a wide divergence in the properties of bras from those of either copper or zinc.

In the main, however, it has to be recorded that th chemical properties of brass follow somewhat in th wake of those of copper. The metal is fairly stable i a dry atmosphere but tarnishes in moist air, giving i warm rooms discolorations which are either brown o black, while in exposed positions green patinas of basi copper carbonate frequently result.

Towards acids, the alloys behave in a manner which i influenced by composition. One would expect an allo rich in zinc to behave somewhat like zinc and to turn ou copper from its salts, while those brasses with a pre ponderance of copper should be fairly stable to coppe salts. This anticipation would be true, and withou

entering into detail as to the several metallurgical constituents of brass it may in a general way be said that in this respect, alloys with more than 50 per cent of copper are stable in copper salts, while those with more zinc precipitate copper.

Towards acids, brass dissolves in a manner which is an average of the behaviour of the constituents. Of the two metals zinc is the more active and more easily attacked. Superficial attack of acid removes zinc, and leaves copper, and thus produces a reddening of the metal. This is an everyday observation, but it is equally evident that such an attack must soon cease, as, superficially, copper soon predominates on the surface and zinc is more difficult of access. Thus in the long run the brass is dissolved away, but there is always a slight red film on the surface. The metal is much too intimately mixed to allow the acid to penetrate the metal and dissolve away the whole of the zinc. This reddening effect may easily be produced by rubbing brass with hydrochloric acid.

Conversely, ammonia has a superior affinity for copper, which in the presence of air is rapidly dissolved by it. Zinc is much less affected, and hence rubbing with ammonia leads to a superficial film of metal containing an excess of zinc and therefore paler in color.

Colors on Brass.—Now it is almost impossible to make any safe prediction as to the behaviour of the different brasses in the endless variety of solutions available for metal coloring. The influence of even traces of impurities on the coloring of copper has already been referred to. There is a general darkening effect, and this, in many cases, becomes very pronounced in the case of brass. This is particularly noticeable in cases in which

copper oxide forms the coloring film. Ammoniacal solutions have little effect on copper, but much effect on brass. The ammonia solutions deposit black oxide on brass and red oxide on copper. This is at least one example of the greater activity of brass than that of copper.

Again, an alloy which in industry is of such variable composition as brass will present some difficulty in the exact reproduction of desired shades. Even the preliminary cleaning operations will have some influence in this direction. As has been pointed out, acids and alkalis variously attack the surface of brass exposed to them and leave behind a film of metal which may vary in composition from the main alloy.

Metallurgically considered, brass is a complex material. While high copper and high zinc brasses act somewhat on the lines of their chief constituents, the usual range of industrial brasses must not be considered to be constituted of individual particles of the two metals more or less carelessly mixed. They are so very intimately mixed that they are not recognisable as separate constituents under the microscope, and thus it happens that the color produced upon them may not agree with those which might be anticipated.

While variations of composition add scope to coloring processes, they also add some difficulties in the exact reproduction of colors.

Black Shade.

Solution :—

Copper sulphate . .	4 ozs.	25 grms.
Water	1 gal.	1 litre
Ammonia (·880) . .	q.s.	q.s.

Dissolve the copper sulphate in the water. The slight urbidity (occasioned possibly by chalk in the water) is mmaterial. Add ammonia (·880) until the green precipiate ($Cu(OH)_2$) first formed is nearly redissolved. A deep blue solution is obtained. The color to be produced is n oxide of copper. It is soluble in ammonia and therefore cannot form in the presence of an excess of this eagent. The slight precipitate left is a guarantee that mmonia is not present in excess. The best results are btained with the solution hot—about 200° F. (93° C.). At this temperature ammonia is being lost by evaporaion and black copper oxide is precipitated. This veakens the solution, hence make further small additions f ammonia, always leaving some precipitate at the ottom of the vessel.

The article for coloring is cleaned as outlined in Chapters V and VI. For a bright finish scour before coloring with whiting and lime, rinse, pass through the yanide dip, rinse well and immerse in the coloring olution. A good deep black color should be produced n a few seconds. Remove, rinse and pass momentarily hrough the following solution :—

Caustic potash . .	2½ ozs.	16 grms.
Water	1 gal.	1 litre

This serves to fix the color. Rinse in cold water, then n hot water and dry off in hot boxwood sawdust.

A bloom may form on the surface. This may be emoved by lightly wiping with a soft cloth, or by a light ouch on a swansdown mop. Lacquer with a transparent acquer, or one with a black shade, to protect from atmospheric corrosion. Dry scratch-brushing before lacquering uts down the color and gives a paler shade.

Should the color be patchy, dry scratch brush and return to the coloring solution. If this is unsuccessful remove the whole of the color by mopping, and after cleaning repeat the coloring process.

Slate-Black on Brass.

Solution I :—

Copper nitrate . .	16 ozs.	100 grms.
Water	1 gal.	1 litre

Solution II :—

Potassium sulphide (Liver of sulphur) .	1 oz.	6·25 grms.
Hydrochloric acid . .	4 ozs.	25 ,,
Water	1 gal.	1 litre

Immerse the cleaned article in Solution I for a few seconds, remove and allow to dry. Then immerse in Solution II, which acts as a developer, remove and dry by heat. Avoid "burning" the color. Finish by dry scratch-brushing with a fine wire brush. Lacquer with transparent lacquer.

Steel Bronze.—This effect is usually obtained by deposits of arsenic on the metal. In general, the solutions are made by dissolving white arsenic (arsenious oxide As_2O_3) in hydrochloric acid. Arsenious chloride ($AsCl_3$) is then present in the solution, from which many metals deposit arsenic by simple immersion.

$$As_2O_3 + 6HCl = 2AsCl_3 + 3H_2O$$
$$2AsCl_3 + 3Cu = 3CuCl_2 + 2As$$

The deposit of arsenic is, however, only very thin, by no means as thick as could be obtained by electro-deposition, for when once the brass is covered with a thin film of arsenic, no further action can occur.

Solution A :—

White arsenic . .	13 ozs.	80 grms.
Hydrochloric acid (coml.)	1 gal.	1 litre

Warm the acid and add the white arsenic. It readily dissolves. *Avoid breathing the fumes which are highly poisonous.* The solution works slowly when cold, but much more satisfactorily at 160° F. (70° C.). The shade is deepened by the addition of ammonium chloride (sal-ammoniac, NH_4Cl) to the extent of twice the weight of the arsenious oxide.

Solution B :—

White arsenic . .	20 ozs.	125 grms.
Copper sulphate (powdered) . .	10 ,,	62 ,,
Hydrochloric acid . .	1 gal.	1 litre

Dissolve the white arsenic in the warm acid as before. Then add the other salts. Stir well. Allow to stand for twelve hours before using. The solution works well cold. No simple explanation seems to be forthcoming of the increased effect due to the copper sulphate.

Solution C :—

Potassium cyanide . .	5 ozs.	32 grms.
White arsenic . .	2 ,,	13 ,,
Water	1 gal.	1 litre

Dissolve the " cyanide " in the water and heat to boiling. Add the white arsenic. Stir well. Use the solution hot.

Electrical Steel Bronze.—This is effected by electro-deposition from the following solution :—

White arsenic . .	2 lbs.	200 grms.
Single nickel salts . .	4 ozs.	25 ,,
Copper sulphate . .	½ oz.	3 ,,
Hydrochloric acid . .	1 gal.	1 litre

Warm the acid and add the several salts. Cool. Pass a current from nickel anodes on to the metal to be colored, using a P.D. of 2–3 volts. Remove when a satisfactory shade is obtained. Rinse well, first in cold water, then in hot water. Dry in hot sawdust, finish on a soft mop with dry lime or rouge. Lacquer to preserve the color.

Various Shades.—Some very good colors may be obtained on brass in the following way :—

Solution :—

Sodium thiosulphate (" Hypo ")	12 ozs.	75 grms.
Lead acetate	8 ,,	50 ,,
Water	1 gal.	1 litre

The two salts are added to the water and the temperature raised to 180° F. (82° C.). The effect is almost immediately observed on suitably cleaned brasswork. A pale gold shade is followed in quick succession by dark gold, orange, brown, crimson, purple and various iridescent shades to pale blue, which finally changes to steel-bronze shade. Close observation is necessary to obtain any single desired shade owing to the rapidity of the changes. Various shades may be obtained on one piece of work by first obtaining the blue shade, relieving in parts down to the brass and then returning to the solution to attain the required shade. Rinse in cold and then hot water. Dry in hot boxwood sawdust, wipe over with a soft cloth and finish with wax brush or transparent lacquer.

The chemistry of this process is fairly well known. When " hypo " is added to lead acetate a white precipitate of lead thiosulphate is first formed :—

$$Pb(C_2H_3O_2)_2 + Na_2S_2O_3 = PbS_2O_3 + 2NaC_2H_3O_2$$

This is soluble in excess, $Na_2S_2O_3$, forming a double salt, $PbS_2O_3 \cdot Na_2S_2O_3$. On heating, this is decomposed and lead sulphide is thrown down, thus :—

$$PbS_2O_3 + H_2O = PbS + H_2SO_4$$

The acid is absorbed by $Na_2S_2O_3$ evolving SO_2 and precipitating sulphur.

$$H_2SO_4 + Na_2S_2O_3 = Na_2SO_4 + H_2O + SO_2 + S$$

The colors are due to films of PbS of increasing thickness. Light passes through the thin films and is reflected from the bright metallic surface beneath the film. The striking color effects are lost when the film attains such a thickness as to carry opacity.

River-clay Yellow.—A peculiar shade resembling that of yellow clay and suitable for clock work and similar ornaments may be produced as follows :—

Solution I :—

Ammonium sulphide .	16 fl. ozs.	100 c.c.
Water	1 gal.	1 litre

Brush solution over the cleaned work and allow to dry. When dry, brush loose sulphur from the surface and dry scratch-brush to tone off color. Repeat the process if necessary.

A somewhat different shade may now be produced by passing through

Solution II :—

Arsenious sulphide (As_2S_3)	8 ozs.	50 grms.
Ammonia (·880) . .	40 fl. ozs.	250 c.c.
Water	1 gal.	1 litre

This solution may also be used separately.

Solution III :—

Antimony sulphide (Sb_2S_3)	16 oz.	100 grms.
Ammonium sulphide .	1 gal.	1 litre

The solution is applied by brushing on to the metal and allowing to dry, repeating the process as may be necessary to obtain up to dark brown shades. The color should, in all cases, be toned with a soft dry wire scratch brush.

Umber-Brown.

Solution :—

Barium sulphide . .	2 ozs.	12½ grms.
Water	1 gal.	1 litre

Use the solution at 120° F. (50° C.). Immerse clean brass until the desired shade is obtained. Remove and rinse in cold, then in hot water and dry out in sawdust. The shade may be varied by varying the proportion of barium sulphide from ½ oz. per gallon up to 2 ozs. per gallon.

Barbedienne Bronze.

Method I :—

Antimony sulphide . . .	1 oz.
Red oxide of iron . . .	3½ drams.

Mix to a thin cream with ammonium sulphide. Apply to work with a brush and allow to dry. Remove loose powder with a dry medium bristle brush. Tone with a dry soft wire scratch brush and lacquer.

Method II :—

Solution A :—

Copper sulphate . .	8 ozs.	50 grms.
Water	1 gal.	1 litre

Solution B :—

Potassium sulphide .	2–4 ozs.	12½–25 grms.
Water	1 gal.	1 litre

Immerse the cleaned work in Solution A at 180° F. (82° C.) until an iridescent green color is obtained. This is a quick effect. Rinse in clean cold water. Now pass for a few seconds through Solution B, used cold. Rinse in cold and then hot water. A deeper tone is obtained by a second immersion in Solution B. The effects vary with the quality of the brass, and the A solution may be varied in strength to meet these changes.

Tubes and brazed articles are troublesome on account of the joints. They should be first plated with brass or copper, but something more than a mere film of plated metal will be required, and the deposits should be scratch-brushed before coloring. This leads to a better finish.

Method III :—

Use Solution A of the previous method. After rinsing, pass the work through :—

Sodium thiosulphate .	8 ozs.	50 grms.
Lead acetate . .	2–4 ,,	12½–25 ,,
Water	1 gal.	1 litre

this solution being kept boiling. Rinse in cold water and re-immerse in the copper solution. The work may be passed from one solution to the other, always with intermediate rinsings to obtain the desired color. Finally, rinse in cold and then hot water, dry off in sawdust, dry scratch brush and lacquer.

Architectural Bronze.—This is a valuable color with a pleasing effect in combination with certain classes of furniture.

Solution :—

Potassium sulphide .	2 ozs.	12½ grms.
Water	1 gal.	1 litre

Use solution at 180° F. The carefully cleaned article is immersed for a few seconds to attain a deep orange shade. Rinse in cold, then hot water and dry in hot boxwood sawdust. Tone off with a soft wire scratch brush and lacquer. Darker shades may be obtained by the use of a solution of about double the above strength.

A similar effect is obtained by plating a very thin film of bright copper from the cyanide bath and, after rinsing, passing through a very weak and cold solution of potassium sulphide. A warm solution gives a deeper tone, which is also affected by the length of immersion. Finish off after drying with soft scratch brush and lacquering.

Flemish Bronze.

Solution :—

Arsenious oxide . . .	1–2 drams
Hydrochloric acid . . .	2 fl. ozs.
Potassium sulphide . . .	½ dram
Water	1 gal.

Dissolve the white arsenic in the acid. Add the solution to the water, finally adding the liver of sulphur. Use at a temperature of 160° F. The desired color should be obtained on properly cleaned brass after only a short immersion, and is finished in the usual manner.

Oak Bronze.—A shade which tones with oak furniture.

Solution :—

Antimony sulphide .	2 ozs.	12½ grms.
Caustic soda . . .	4 ,,	25 ,,
Ammonia (·880) . .	¼ fl. oz.	1·5 c.c.
Water	1 gal.	1 litre

Use solution at 160° F. The color should be attained in a very short time, and the work is then rinsed in cold and hot water.

The color can be darkened by passing the work through either of the following toning solutions :—

A.	Hydrochloric acid or sulphuric acid . .	1 oz.	6¼ grms.
	Water . . .	1 gal.	1 litre
B.	Copper sulphate . .	2 oz.	12½ grms.
	Water . . .	1 gal.	1 litre

Prior to using these toning solutions the colored article is dry scratch-brushed. The final shade depends upon the length of immersion in the toning solution. Rinse, dry in sawdust and finish on dry scratch brush. If the color is unsatisfactory, completely remove it by mopping or dipping and recolor.

Chocolate Color on Brass.

Solution :—

Copper sulphate . .	4 ozs.	25 grms.
Double nickel salts . .	4 ,,	25 ,,
Potassium chlorate . .	4 ,,	25 ,,
Water	1 gal.	1 litre

The solution is used boiling, the work, cleaned in the usual manner, being treated by immersion. Preliminary unsatisfactory results may be removed by wet scratch-brushing, or by drying and dry scratch-brushing.

CHAPTER XIII

COLORING OF BRASS (*cont.*)

Parcel Plating and Coloring.—It has already been seen that markedly different colors are produced on copper and brass in some solutions. Artistic effects may thus be produced by including both metals in a single piece of work. While it may not be easy to embody the two metals in the construction of articles, it is a comparatively simple matter to deposit copper upon parts of a piece of brass. The process is called "parcel plating," and is applicable to all deposited metals.

For parcel coppering on brass the article is thoroughly cleaned in the usual manner and dried. A design is then drawn on the surface of the brass with a fine pencil brush, using best copal varnish mixed with a little asphaltum. In the case of figured designs it is a simple matter to "stop off" a portion of the design. When the varnish is dry and hard, the exposed parts are coppered in the acid sulphate solution for from half an hour to an hour. After rinsing and roughly drying, the varnish is removed with turpentine and the brass thus exposed. If coloring is not required the article can be cleaned from the turpentine, potashed, scratch-brushed and finished with grease and lime on a cotton mop and lacquered.

For coloring, a solution of copper nitrate may be used.

Solution :—

Copper nitrate . .	5 lbs.	500 grms.
Water	1 gal.	1 litre

After removal of the " stopping-off " varnish the work is potashed, scratch-brushed and immersed in the coloring solution at 120° F. The colors soon appear, the brass assuming a nearly black shade, while that on the copper is brown. The two shades provide a pleasing contrast. Another solution which may be used with good effect is that given on page 156 for black on brass, the copper simultaneously assuming a red to brown color. Other solutions may also be used.

In carrying out the stopping-off process, natural effects should be aimed at. In figures or figured articles, draped parts should be stopped off and copper deposited on exposed parts. Flowers should be treated to give, as far as possible, natural shades. Autumn tints and sunset shades may be produced on suitable subjects by a skilled operator. Deposition of copper, brass, nickel, silver and gold may be effectively used.

Sheffield Bronze.—This is another shade of brown.

Solution :—

Arsenious sulphide	20 oz.	125 grms.
Antimonious sulphide	20 ,,	125 ,,
Ammonium sulphide	1 gal.	1 litre

These reagents are digested together, the solids being in excess leaving a slight residue, the bulk of them dissolving. The solution contains ammonium thioarsenite, NH_4AsS_3, and ammonium thioantimonite, NH_4SbS_3. It is worked at 95° F. In it the cleaned article soon assumes a brownish shade, due to the formation of a film of mixed sulphides. If the film is patchy it may be removed by scratch-brushing, and the work re-immersed in the solution. When a satisfactory effect

is obtained the usual methods of finishing and lacquering are followed. The solution cannot be kept for any length of time.

Yellowish Green Patina.

Solution :—

Ammonium chloride .	3½ lbs.	350 grms.
Copper acetate . .	2 ,,	200 ,,
Water	1 gal.	1 litre

Special preparation of the work for receiving a patina involves smoothness for the high lights and dullness for the low lights. Polishing may be applied for the former and sandblasting for the background. The prepared work is brushed with the solution and allowed to dry for twenty-four hours. A fine yellowish green results on the smooth portions, with a denser effect on the rougher portions. The high lights may even then be lightly rubbed over with a soft leather or velvet moistened with beeswax compound, made by dissolving beeswax in turpentine with a few drops of olive oil. Very little is required to give the best effect. The exact finish is a matter for the operator's judgment, but will vary with the class of work under treatment. The method is particularly suitable for cast brass.

Apple Green Patina.

Materials :—

Sodium chloride . .	20 ozs.	125 grms.
Ammonia (·880) . .	16 fl. ozs.	100 c.c.
Ammonium chloride .	20 ozs.	125 grms.
Vinegar . . .	1 gal.	1 litre

The prepared work is evenly painted with the mixture

and allowed to dry for twenty-four hours, being subsequently finished as in the previous case.

Old Abbey Green.

Solution :—

Arsenious oxide . .	2 lbs.	200 grms.
Ammonium chloride .	12 ,,	1200 ,,
Verdigris . . .	12 ,,	1200 ,,
Copper carbonate . .	4 ,,	400 ,,
Hydrochloric acid . .	1 gal.	1 litre

The arsenious oxide is dissolved in the hydrochloric acid (the fumes must not be inhaled) and the remaining materials stirred in and boiled for 15 minutes. The mixture is allowed to settle for 10 hours, and is then applied to the article with a brush. Further applications may be made after periods of 15 minutes until the desired shade is obtained, and the article finished as in the case of the yellowish green patina above. Cast brass and copper give the best effects.

Bluish Green.

Solution :—

Sodium thiosulphate .	1 oz.	$6\frac{1}{4}$ grms.
Pernitrate of iron . .	8 ozs.	50 ,,
Water	1 gal.	1 litre

The cleaned work, which, according to taste, may be either bright or dead, is immersed in the solution at 180° F. The desired shade appears in a few seconds, after which, finishing processes include, in order, rinsing in cold and hot waters, drying in sawdust, wiping with a soft cloth to remove dust and lacquering with a green-tinted lacquer. Very uniform effects are obtained on electrolytically deposited brasses.

Olive-Green.

Solution :—

Nickel ammonium sulphate	8 ozs.	50 grms.
Sodium thiosulphate .	8 ,,	50 ,,
Water	1 gal.	1 litre

The solution is used at 150° F., the "hypo" being added subsequently to the solution of the nickel salt. The brass surface must be scrupulously clean, and the color appears a few seconds after immersion. The shade may be varied with the proportion of "hypo," larger amounts of this salt giving darker effects. Temperature and time of immersion also influence color. When the required shade is obtained the usual finishing is resorted to, lacquering with a green-tinted lacquer.

Antique Green.

Solution :—

Copper sulphate . .	12 ozs.	75 grms.
Ammonium chloride .	2 ,,	12½ ,,
Water	1 gal.	1 litre

Dissolve the copper salt and then add the ammonium chloride. Use the solution nearly boiling, say at 200° F. A dull dead shade will be obtained in a few seconds. The quantity of ammonium chloride needs most careful control. An excess produces an easily removable deposit, while too little gives a brown shade. If an unsatisfactory shade is produced, completely remove by scratch-brushing and re-immerse, after making any necessary correction to the amount of ammonium chloride present.

After obtaining a satisfactory shade rinse in cold, then in hot water. Dry in sawdust and complete drying in air oven at 100° F. to eradicate moisture from the pores of

a casting. High lights are now relieved by rubbing with a paste of beeswax in turpentine with a mere drop of olive oil. The same paste is applied with a camel-hair brush to the low lights, and the article is kept for about 15 minutes at 100° F.

Fern Green.

Materials :—

Copper sulphate
Ammonium chloride } in equal quantities.
Lead acetate

These are crushed together to secure intimate mixture, and mixed with water to a paste which should be further ground until quite smooth. Apply the paste evenly and smoothly with a brush and allow to dry—the slower the better. During drying remove unequal quantities of paste and more evenly distribute the paste if necessary. When the paste is dry and hard the work is again raised to blood-heat—98° F.—in an oven and well brushed with a medium stove or bristle brush, applying more pressure on the high lights and little on the low. The work is finally rubbed on the high lights with a soft pad of leather or velvet with wax composition. This will suitably polish the prominent parts, while the background is merely dusted with a soft brush. Lacquering is now resorted to with a lacquer having sufficient green color to somewhat improve the appearance.

To give a bronze shade the same materials may be used as follows :—

Copper sulphate . .	4 ozs.	25 grms.
Ammonium chloride .	4 ,,	25 ,,
Lead acetate . .	4 ,,	25 ,,
Water	1 gal.	1 litre

When dissolved, stir, and immerse the cleaned work when the solution is at 180–200° F. About one minute should suffice to give the color, but if unsatisfactory it may be removed and the process repeated until a good brown color of pleasing shade is obtained, after which the usual rinsing, drying and dry scratch-brushing are followed by lacquering with a transparent or copper-tinted lacquer.

Statue Green Patina.

Mixture :—

Calcium chloride . .	20 ozs.	125 grms.
Ammonium chloride .	20 ,,	125 ,,
Water	1 gal.	1 litre

The materials are dissolved and the solution strained through coarse calico (cheap calico, well washed, will answer the purpose). The solution is applied to the figure evenly with a soft brush and the work set aside to dry, being touched up from time to time to guarantee a uniform surface. When dry and hard, warm to about 100° F. and rub down the high parts with a soft waxed brush, using beeswax composition. Variations of the method may be made as follows :—

1. A very light film of copper may be deposited before coloring. A somewhat different tone is obtained thereby.

2. Pass the work, after the above treatment, through the following solution :—

Potassium sulphide .	2 drs.	·8 grm.
Water	1 gal.	1 litre

After coloring rinse, dry and finish with wax and lacquer. The best results in all cases demand care and patience.

Orange Tint.

Solution :—

Caustic soda . . .	4 ozs.	25 grms.
Copper carbonate . .	8 „	50 „
Water	1 gal.	1 litre

The cleaned article is immersed in the solution at 160°–180° F. for the required length of time necessary for the desired shade. Both the time of the immersion and temperature of the solution influence the shade, which may vary from a pale gold to a deep orange. When colored, the usual rinsing and drying is followed by wiping with a soft cloth and lacquering with a transparent or pale gold lacquer. The surface of the article should be, before coloring, perfectly free from grease and oxide.

Tasmanian Brown.—Very pleasing—indeed beautiful—shades of brown may be produced on brass by immersing in the following solution :—

Potassium sulphide . .	2 ozs.	12·5 grms.
Barium sulphide . .	4 „	25 „
Ammonia (·880) . .	8 fl. ozs.	50 c.c.
Water	2–5 gals.	2–5 litres

The solution is used at 200° F. and the shade varies with the strength of the solution. Alternative shades may be obtained by giving the work a thin film of copper and well scratch-brushing before coloring in the solution. When a satisfactory shade has been obtained the work is finished by rinsing, drying, dry scratch-brushing to equalise the shade, and lacquering with a transparent lacquer.

Greenish Brown Shade.

Solution :—

Potassium sulphide . .	½ oz.	3 grms.
Ammonium sulphide .	½ fl. oz.	3 c.c.
Water	1 gal.	1 litre

This solution at a temperature of 80° F. is used as an electrolyte with a iron or steel anode and the cleaned work as cathode. The current may be of the order of 10–20 amperes per sq. ft. A short treatment—about three minutes—should suffice, and the process repeated if necessary after removing by scratch-brushing any defective result. The correct color being obtained, the work is finished in the usual manner, using a transparent lacquer. The method is suitable for small work such as buttons.

Tudor Bronze.

Solution :—

Antimony sulphide (fresh) .	4 ozs.	25 grms.
Caustic soda . . .	8 ,,	50 ,,
Ammonia (·880) . .	½ fl. oz.	3 c.c.
Water	1 gal.	1 litre

After careful preparation the work to be colored is immersed in this solution at 160° F. A few seconds' immersion will suffice. The color may then be toned and darker shades obtained by passing the work, subsequent to coloring, through one of the following :—

Toning Solutions :—

1. Sulphuric acid or hydrochloric acid . .	2 fl. ozs.	12·5 c.c.
Water . . .	1 gal.	1 litre
2. Copper sulphate . .	4 ozs.	25 grms.
Water . . .	1 gal.	1 litre

These solutions are used cold.

It will be found that there is room for variation of shade by alteration of the conditions, such as the temperature of the coloring solution and the period of immersion

in both the coloring and the toning solution. The colors can be removed by the scratch brush and the operations repeated if found necessary, and the work finished by the usual procedure, using transparent lacquer.

Antiquate Green.—This is an antique result obtainable on cast or undercut articles or figured work where relief will add to the beauty.

Solution A :—

Acetic acid	1 vol.
Ammonium carbonate (saturated solution)	30 vols.

Warm the solution to 80–100° F. and apply to the work either by brushing or by immersion. The solution, however applied, must be evenly distributed, otherwise a patchy result will be obtained. It is allowed to dry slowly. Quick drying leads to a loose colour.

Solution B :—

Acetic acid . . .	8 fl. ozs.	48 c.c.
Ammonium carbonate .	4 ozs.	24 grms.
Cream of tartar . .	1 oz.	6 ,,
Sodium chloride . .	1 ,,	6 ,,
Copper sulphate . .	1 ,,	6 ,,
Water	2 fl. ozs.	12 c.c.

Well grind the solid materials together and add the liquid constituents to produce a paste. This is applied to the surface at 80–100° F. and allowed to slowly dry, taking from 12–48 hours. Slow drying improves the result. The work should be inspected during drying to avoid the liquid collecting as drops. When dry, heat up to 100° F. for 15 minutes. Remove and relieve by

rubbing the high lights with a soft leather pad moistened with a few drops of olive oil, sufficient to develop a polish without leaving the surface distinctly greasy. Further treatment involves the application of a mixture of chrome yellow (lead chromate) and ammonia, or ferric oxide and ammonia to the prominent parts. Finish with a beeswaxed brush. Careful work, patiently done, will reward the operator with a first-class result. It is fatal to good work to hurry the process.

Green Verde.

Solution :—

Copper nitrate . .	5 ozs.	32 grms.
Ammonium chloride .	5 ,,	32 ,,
Chloride of lime . .	5 ,,	32 ,,
Water	1–2 gals.	1–2 litres

The solution is used at 75° F. It gives a result direct on brass, but a much more satisfactory verde green is obtained if the brass is very lightly coppered. Before immersion in the coloring solution slightly "oxidise" the surface by passing through a solution of :—

Barium sulphide, potassium sulphide or ammonium sulphide	$\frac{1}{4}$ oz. per gal. of water or $1\frac{1}{2}$ c.c. per litre

These solutions are used cold for light shades and warm for dark shades.

A final deeper green is obtained with a thicker copper deposit passed through a preliminary oxidising solution used warm and made up as follows :—

Potassium sulphide	2 ozs.
Ammonium chloride . . .	4 ,,
Water	1 gal.

This preliminary treatment should give a black or nearly black film firm enough to stand dry scratch-brushing. The work is now colored by a rapid immersion in the coloring solution. It is withdrawn and allowed to drain and to dry, when the color will form in a few hours. When dry and well set, the finish may be obtained by relieving and waxing, or lacquering.

Rich Antique Green.—This effect is produced by pigments applied to a dead or matt surface obtained by sandblasting or similar method.

Solution :—

Ammonia . . .	40 fl. ozs.	250 c.c.
Copper carbonate. .	2 lbs.	200 grms.
Sodium carbonate .	2 ,,	200 ,,
Water . . .	1 gal.	1 litre

The solution is used warm and applied by brushing over the work or by immersion as may be more convenient. This solution darkens the surface to give a good tone to the final green. Wash in clean hot water, dry in hot sawdust, dust off and lacquer.

The lacquer for this purpose is composed of French varnish diluted with alcohol. To this is added equal parts of fusel oil and amyl acetate. These are thoroughly mixed and applied to the article with a fitch varnish brush or spray and dried for 5–10 minutes at a moderate temperature.

The green pigment is composed of :—

White zinc (dry) or
White lead.
Chrome green and a trace of blue coloring.

These are mixed to a thin paste with turpentine con-

taining a little copal varnish. The mixture is carefully applied with a camel-hair brush to produce a lustreless opaque surface. Any appearance of the pigment having been painted on must be rigidly avoided. Particular attention is given to the low lights. This done, the article is warmed on a hot plate or in an oven for 10–15 minutes to soften the lacquer and allow the pigment to penetrate. Again the work is allowed to stand in order to dry and harden.

A mixture of lampblack and chrome yellow is made and applied with a brush already moistened with a mixture of copal varnish and turpentine. After having obtained a satisfactory color by trial with the mixture, it is applied to the work by a gentle backward and forward motion which will cause the color to adhere on the high lights and give a metallic finish. The work is now dried in a stove and, after cooling, finished by rubbing the high lights with a soft cloth so that the brass shows through. Another light touch with the pigment brush gives an old-brass appearance. After drying, the work is again polished with a soft wash leather, or velvet pad very slightly lubricated with a drop of olive oil, to obtain the final old-brass appearance.

Bronze Tones.

Pigment Method :—

Solution :—

Antimony sulphide (yellow)	2 ozs.	12½ grms.
Caustic soda . . .	4 ,,	25 ,,
Ammonia (·880) . .	¼ fl. oz.	1½ c.c.
Water	1 gal.	1 litre

The solution is used at 160° F., and the cleaned article

immersed for a few seconds. A dark greenish shade appears, after which the work is rinsed.

The color is now darkened by toning in one of the following solutions :—

(*a*) Hydrochloric acid or sulphuric acid .	1 fl. oz.	6 c.c.
Water . . .	1 gal.	1 litre
(*b*) Copper sulphate .	2 ozs.	12½ grms.
Water . . .	1 gal.	1 litre

After toning, the work is rinsed and finished off in the usual manner. It is now ready to receive the ground-work of the pigment coloring. The work will be subsequently lacquered, but before doing so the coloring pigments should be prepared. These may be purchased to the required shade or prepared from such primary colors as zinc white, the chromes, etc. The colors should be thoroughly mixed and in a finely powdered form. The work is now lacquered with a good air-drying lacquer, and before quite dry the pigment is dusted on with a soft wash leather. This is done quickly while the lacquer is still "tacky," and the drying of the lacquer is now completed, after which superfluous powder is dusted off. Parts, such as may be required of a darker shade, are relacquered and retreated with the powder, and the high lights receive a light polishing with a soft piece of velvet. A very pleasing effect should be obtained.

By *another method*, lacquering and drying hard at 100° F. are resorted to. The appropriate colors, such as greens, blues, yellows or blacks, are mixed to a paint consistency with turpentine containing copal varnish to the extent of 1 fl. oz. per pint. This mixture is evenly

applied to the work by means of a soft brush and then allowed to dry. Relieving may then be applied by a rag or wash leather dipped in turpentine mixed with an equal volume of boiled linseed oil.

A crystallised effect may be produced by using the pigment, much more diluted with turpentine, containing copal varnish to the extent of 1½ fl. oz. per quart. The preparation is "stippled" on to the article by means of a stippling brush. A rose-gold effect may be produced from a mixture of orange chrome and finely divided oxide of iron (the finest quality of jewellers' rouge). Similarly, soluble blue and oxide of iron give the Venetian bronze tones. Having obtained the required shade, finishing is effected by a fine hair brush with the application of a little wax.

Lustre Shades.

Solution :—

Cream of tartar . .	1 oz.	6 grms.
Tin perchloride . .	½ ,,	3 ,,
Sodium bisulphite . .	3 ozs.	19 ,,
Water	1 gal.	1 litre

The salts are dissolved in separate parts of the water. The tin solution is added to the cream of tartar solution and the mixture, after boiling, is allowed to settle. The clear liquid is poured off into the "bisulphite" solution and, after again boiling, the mixture is filtered through calico. Care is required in the preparation of this mixture.

Highly polished brass will, when immersed in the hot solution, give (according to temperature and time of immersion) various shades from light gold to brown. The work is finished with a transparent lacquer.

Electrolier Grey.—This is suitable for electric light and gas fittings.

Solution :—

Arsenious oxide . .	5 ozs.	31 grms.
Caustic soda . . .	12 ,,	75 ,,
Water	1 gal.	1 litre

The caustic soda is dissolved in a little of the water (warmed) and the white arsenic added, a little at a time with stirring. When dissolved add the remainder of the water and allow to cool.

In this solution the cleaned work is made cathode. An anode of steel or brass is used and a current at 3–4 volts passed for about 5 minutes. A grey deposit of "metallic" arsenic is obtained. The solution will conduct the current better by the addition of a small proportion of cyanide ($\frac{1}{2}$–1 oz. per gallon). Rinse and dry. Scratch-brush with a fine steel wire brush and lacquer with transparent lacquer.

Cloud Brass Finish or Smoke-bronze.—This finish is mainly applied for art metal work. A bright surface gives a china finish, while on a matt surface an opaque or egg-shell finish is obtained.

A matt surface may be produced by (1) sandblasting, (2) acid dipping (see page 71) or (3) scratch-brushing with a coarse brush and pumice powder. The prepared surface must be free from stains and perfectly dry. A slow-drying varnish is then evenly applied to the surface, and during drying, while the varnish is still in a "tacky" condition, the surface is held over a smoky flame so that the deposited soot adheres to the varnish and is retained by it while drying. There is scope here for artistic treatment in shading. In a figure, the low lights may be

blackened while the high lights are given only a smoky brass appearance. The shading can best be controlled in a darkened room, and a revolving table is an aid to the operator. A cylindrical article may be centred in a lathe or other convenient rest and a smoky flame applied from a flexible gas attachment. In plain work the denser deposit should be applied at the bottom, carefully shading off upwards. Careful handling of the article is essential. When the varnish has then been allowed to set hard the work is immersed in, and carefully withdrawn from, the lacquer and allowed to drain and dry and harden at 100° F.

The same smoke treatment applies for bright surfaces, but shading is rather more difficult. Various shadings may be given by the use of colored lacquers of shade suitable to the work in hand.

A **Light Brown** shade sensitive to light is obtained on brass as with copper (see page 148). It is possible to obtain a colored film sensitive to light, the successful fixing of which has not yet been achieved. The effect of light is to change a light brown into a dark green or nearly black shade.

Materials :—

Copper sulphate
Zinc chloride
} equal weights

These are mixed together with sufficient water to produce a thin paste, which is spread evenly over the surface with a brush. The paste is allowed to dry and then removed by washing, first in cold water and then hot, drying out in sawdust, toning with a scratch brush and lacquering. Exposure to bright light then effects the change of color

to dark green. A brass plate treated by this method may be used as a printing paper over a negative.

Optical Black.—A dull black is frequently required on the inside of brass tubes in telescopes, microscopes and other optical instruments. Several methods are available for this purpose.

Method I.—The inside of the tube, first properly cleaned, is mopped with a wad of wool wetted with either (*a*) silver dissolved in nitric acid, (*b*) a mixed solution of copper and silver nitrates or (*c*) a solution of copper nitrate. The color thus obtained may be deepened by further applying a solution of potassium sulphide and, after rinsing, drying off in sawdust.

Method II.—Equal quantities of tin proto-chloride and gold chloride ($AuCl_3$) are dissolved in water and the solution applied to the cleaned surface by means of a piece of rag. In the absence of an excess of free acid (assuming the gold chloride to have been prepared by dissolving the metal in aqua regia) a durable dead black results.

Method III.—A solution of bismuth nitrate ($Bi(NO_3)_3$) may be applied at 100° F. and yields a deep brown color.

In applying these methods, silver solutions must be mixed with distilled water. Gold and silver solutions must not be too strong, otherwise loose and easily peeled black deposits result. These solutions must be used with economy on account of the cost of materials.

CHAPTER XIV

COLORING OF SILVER

Properties of Silver.—Silver provides another example of a metal on which pleasing effects can be produced by simple chemical methods. These may provide strikingly decorative contrasts with what we may reasonably regard as the monotonously white metal. The pure metal is softer than copper, but harder than gold. It may take a brilliant polish. It is exceedingly malleable and ductile, and is in these properties second only to gold. It is so malleable that leaves down to 1 mil. in thickness can be hammered from it, and so ductile that 1 grain of the metal may be drawn down to 400 ft. of wire.

From the colorer's point of view the chemical properties are of more importance. The metal is, in dry and moist air, wonderfully stable if certain impurities are absent. Silver does not directly combine with oxygen, either at ordinary or elevated temperatures. Two oxides, Ag_2O and Ag_2O_2, may be prepared chemically. They are both readily decomposed on heating. They therefore play no part in metal coloring.

At a high temperature, molten silver (m.p. 960° C.) absorbs oxygen without combination. This oxygen is not retained on solidifying. It is expelled as the surface of the metal begins to harden and produces a rough surface. The phenomenon is called "spitting" or "sprouting."

The metal is readily dissolved by nitric acid, and is thus converted into silver nitrate :—

$$3Ag + 4HNO_3 = 3AgNO_3 + NO + 2H_2O$$

The crystals of $AgNO_3$ are readily obtained by evaporation.

While not much affected by dilute sulphuric acid the warm strong acid quickly attacks it :—

$$Ag + 2H_2SO_4 = Ag_2SO_4 + SO_2 + 2H_2O$$

These actions provide methods of separating silver from a relatively smaller amount of gold. The process is called " parting," and is largely practised by gold and silver refiners. The mixture of gold and silver must contain at least 60 per cent of silver, and in the case of an alloy containing less than this amount an addition of silver must be made up to this proportion.

Silver is not appreciably attacked by other acids, and its extensive use in one or other form in tableware is based on its inertness with the many acids usually occurring in foodstuffs.

Silver sulphide, however, is an important silver compound. It occurs widely in nature and provides the chief source of the metal. It is formed whenever the metal comes into contact with either sulphur or many of the sulphides. Direct combination of the two elements readily occurs :—

$$2Ag + S = Ag_2S$$

while the metal quickly displaces hydrogen from sulphuretted hydrogen :—

$$H_2S + 2Ag = Ag_2S + H_2$$

As this gas is a common constituent of air, especially

where the combustion of gas or coal is going on, tarnishing of the silver quickly occurs, due to the formation of a film of the sulphide. Further, the reaction, under control, provides a ready method of coloring silver. The stain is soluble in, among other reagents, potassium cyanide, which thus provides a useful cleaner for silver :—

$$Ag_2S + 4KCN = 2AgCNKCN + K_2S$$

Silver chloride (AgCl) may be noted as the turbidity produced when silver nitrate is mixed with soluble chlorides, some of which occur in ordinary industrial waters :—

$$AgNO_3 + NaCl = AgCl + NaNO_3$$

It is produced as a heavy white curdy precipitate which is readily soluble in potassium cyanide, sodium thiosulphate or ammonia—new compounds in each case being formed ; for example :—

$$2AgCl + 2Na_2S_2O_3 = Ag_2S_2O_3{\cdot}Na_2S_2O_3 + 2NaCl$$

Silver Alloys.—Owing to its softness, silver has little application in the pure form. Small percentages of other metals considerably harden it, but at the same time lower its electrical conductivity. The most common alloy is the standard silver for coinage and other purposes. This contains 92·5 per cent silver and 7·5 per cent copper. Coinage alloys in other countries contain less silver, and the recent coinage in our own country now contains the standard alloy and nickel in approximately equal amounts. While many other alloys of silver are possible, few are used, and the work of the metal colorer will be mainly confined to the standard alloy and the almost pure metal which is deposited in the process of electroplating.

Coloring of Silver.—By "silver" is here meant both silver goods and silverplated work. As a matter of fact, the methods in use for coloring silver are not largely influenced by the presence of small amounts of other metals in the silver. Thus, while standard silver contains as much as 7·5 per cent of copper, the preponderance of silver and its marked susceptibility to coloration in the solutions commonly employed, altogether overshadow the copper.

"Oxidising."—The common method of coloring is that called "oxidising" (abbreviated in the trade to "silver ox"). This is in any case a misnomer. The bulk of the coloring materials used are sulphides, and the colors formed are due to silver sulphide. Sulphuretted hydrogen, ammonium sulphide, potassium sulphide and barium sulphide are amongst these materials. One of them may be taken as typical of the remainder. With sulphuretted hydrogen the following reaction occurs:—

$$H_2S + 2Ag = Ag_2S + H_2$$

while with a solution of potassium sulphide we get:—

$$K_2S + 2H_2O + 2Ag = Ag_2S + 2KOH + H_2$$

In any case a little silver sulphide produces a large coloring effect, owing to the extreme thinness of the film, and no hydrogen will be obviously evolved. The process is thus not one of oxidising in the chemical sense, but rather one of sulphidising, although the term is infrequently used. The same effect is produced when, as may often happen, silver coins come in contact with india-rubber when the sulphur used in vulcanising the rubber—and there is always an excess of sulphur—combines directly with the silver.

"Oxidising" Solution.

1.	Potassium sulphide .	3–4 drs.	1½ grms.
	Water . . .	1 gal.	1 litre

The solution is used at 160° F. Stronger solutions give a quicker color which, however, is apt to rub off. The silverwork is first prepared as for plating, and is bright or dead, or may combine the two effects to choice. It is passed through the solution until a satisfactory tint has been obtained.

Alternative solutions are :—

2.	Potassium sulphide .	½ oz.	3 grms.
	Ammonium carbonate .	1 ,,	6 ,,
	Water . . .	1 gal.	1 litre
3.	Potassium sulphide .	6 drs.	2 grms.
	Ammonium chloride .	1 oz.	6 ,,
	Water . . .	1 gal.	1 litre
4.	Ammonium sulphide .	40 fl. ozs.	250 c.c.
	Water . . .	1 gal.	1 litre

Deeper shades can be produced by using a still stronger solution, such as :—

5.	Ammonium sulphide .	80 fl. ozs.	500 c.c.
	Water . . .	1 gal.	1 litre

Having decided upon the solution to be used the cleaned article is passed through it while warm, and is then rinsed, dried out and dry scratch-brushed. Relieving is now done. If a bright relief is required, a soft swans-down mop is used with tallow and lime or rouge, with enough pressure to just cut through the color. If a dull relief is required this can be obtained by means of pumice powder and water.

Again, a general matt surface may be required. This is attained by first coloring and then sandblasting with

a No. 1 or No. 2 grade of sand. No. 1 will give a fine satin surface, while No. 2 gives a coarser surface. If bright and matt are required side by side, the bright may be protected by a shield of stout gummed paper while the matt surface is being produced. After "matting" the gummed paper can be removed by warm water and the article dried and lacquered. Bright reliefs can be obtained by burnishing some parts after sandblasting others, and these and other variations of treatment can be left to the discretion of the operator.

"Argentine" Antique Bronze, for silver or silverplated ware.

Solution :—

Potassium sulphide . .	4 ozs.	25 grms.
Ammonium chloride . .	6 ,,	38 ,,
Water	1 gal.	1 litre

Used cold, this solution produces an irregular brownish black after a few seconds' immersion. Rinse in cold and hot waters. Dry in hot sawdust. Dry scratch-brush with a fair pressure. Then pass through the following

Solution :—

Barium sulphide . .	$\frac{1}{3}$ oz.	2 grms.
Water	1 gal.	1 litre

A few seconds' immersion at 160° F. completes the process for a pleasing antique appearance on figured work. Lacquer to finish and preserve color.

Various Shades.—Barium sulphide provides a source of very beautiful shades on silver or silverplated articles.

Solution :—

Barium sulphide . .	$\frac{1}{2}$ oz.	3·25 grms.
Water . . .	1 gal.	1 litre

The solution may be used cold or warm. Cold solutions give a golden tint at the start, passing to pale and deep shades of crimson and purple and finally on to brown. At a temperature of 120° F. the color changes follow in rapid succession, and the process is more difficult to arrest at any stage. The final brown tones are, however, very beautiful. A solution of double the above strength yields still quicker results, and when heated to 160° F. blue and black shades appear in a few seconds. Scratch-brushing not only imparts uniformity to the color, but also reduces it.

Use of Platinum Chloride.—Platinum chloride was one of the materials early used in the coloring of silver. It is obviously of high cost, and hence its displacement by less expensive materials which may give at least an equal result. Very dilute solutions, either in water or in alcohol, were employed and the solution applied by a soft brush or rag, or the work passed through. In any case, simple substitution of platinum for silver took place :—

$$4Ag + PtCl_4 = Pt + 4AgCl$$

The color is thus due to a deposit of platinum, small in amount, while the silver chloride formed would also be so small as to be regarded as negligible. A similar but much more protracted treatment was adopted in the preparation of the platinised silver plates of the Smee cell, the microscopically rough deposit disengaging the bubbles of hydrogen and thus reducing polarisation.

Parcel Gilding on Silver.—For the ornamentation of figured work requiring relief in another metal, parcel gilding gives excellent effects on silver.

For this purpose the silver or silverplated work is

cleaned as for plating, and after drying is stopped off with a good varnish which, after application, is dried and hardened. The unprotected parts are then gilt by means of the current passing through a solution, such as that described on page 117. The solution is preferably used warm, richer tones being thereby produced. Quite a thin film will suffice for such coloring purposes.

Alternatively, the gilding solution may be applied to the work (made cathode) by means of a neat pad of cotton-wool or soft rag bound on a platinum wire, which is made anode. Current from a cell, accumulator or dynamo may be used. The pad is then moistened with the gilding solution and slowly passed over the surface to be gilt. It requires resoaking in the solution from time to time, as it can carry but little gold. A small gold anode inside the pad and attached to the platinum may be used, but a copper wire should be avoided, as this metal would be dissolved, and, passing into the limited quantity of solution held by the pad, may soon give rise to a reddish and unsatisfactory deposit.

When the gilding has been successfully accomplished, the stopping-off varnish may be removed, and the surface carefully cleaned preparatory to oxidising the silver by one or other of the processes previously described.

Floral designs lend themselves to beautiful effects by the deposition of copper, silver and gold on different parts, some being burnished while others are left dead, while the necessary green shade may be put on by a lacquer of the desired color. Some very fine shades may be made by dissolving dyes in Zapon thinning liquid and then adding the Zapon transparent lacquer in order to get the necessary consistency, which must admit of easy

manipulation without the risk of flowing on to parts on which it may not be required. Parts required to show up bright must be lacquered on a burnished surface, the lacquer being sufficiently transparent for the sheen of the metal beneath to be blended with the color of the lacquer.

American Silver Tone.—This is a smoke bronze on silver, which can be made to give pleasing effects. The work should first be sandblasted with No. 1 or No. 2 grade of sand according to the finish required. Alternatively, the work may be dressed on a mop. A calico mop is first cleaned by applying a piece of rough brick to it while revolving, or by holding a piece of iron in which holes have been punched, so that the jagged edges press against the mop. The mop is thus cleaned. The edges are then dressed in glue and rolled in emery powder, using 90 for a rough finish and 120 for a finer finish. The mop is then allowed to dry before being used for preparing the work to be colored. This is a tool with which much useful work can be done, and its possibilities will best be realised by some experience in its use.

The prepared surface is next varnished with a good copal varnish. The varnish should flow smoothly and may, if necessary, be thinned with turpentine. It is allowed to dry, but not to harden. Some work may now be mounted so that it will rotate, and a small gas flame is manipulated upon it so as to shade it from olive-green to black. The lower portions are usually shaded more deeply, toning upwards to olive-green. When the shading is completed the work is put on one side to allow the varnish to harden. Where figured articles are being treated, the high lights can now be rubbed through to

the silver. These exposed parts are then touched with a pad soaked in a dilute solution of potassium or barium sulphide (see pp. 188, 189), sponged with clean water, dried and dry scratch-brushed on the high lights. The articles are then given a coating of thin varnish, and when dry a flash only of smoke. If the low lights are very much undercut and are to be finished dead black, smoking will be difficult and a dead black lacquer may be used to good effect. When smoking, care must be exercised to avoid too high a temperature, which will cause the varnish to blister. When a satisfactory finish has been obtained, the work may be gone over with a soft leather or velvet to remove any finger-marks, and after 24 hours' hardening, the work can pass into the packing room.

Cleaning of Silver.—The readiness of silver to tarnish is well known, and it has been pointed out that the discoloration is due to the formation of silver sulphide. Solvents for silver sulphide constitute cleaning agents for silver. Amongst these may be mentioned potassium cyanide and ammonia solutions, while whiting is a most effective reagent.

One method, based on an electrolytic principle, is worthy of mention here. The stained silver is placed in a hot solution of washing soda (say 1 lb. per gallon), and to it is added aluminium, either as a sheet or even scrap pieces. The whole is stirred a little to ensure that the silver pieces come into contact, either directly or through other silver pieces, with the aluminium. They are instantaneously whitened and need only to be rinsed, dried and polished with a soft cloth.

The principle is simple. The aluminium and silver form electrolytic couples, aluminium being the anode

and silver the cathode. The soda solution is, of course, conductive. Currents pass from the anode to the cathodes, dissolving a little aluminium and producing hydrogen on the silver goods. This hydrogen reduces the dark silver sulphide stain to white silver, thus :—

$$Ag_2S + 2H = H_2S + 2Ag$$

Zinc would serve instead of aluminium, but it is not so effective. The consumption of aluminium is very small, and a metal of this character is sold for this purpose. The method is strikingly effective, and experiments have shown that the loss of silver by this method is only one-twentieth of that lost by mechanical methods using whiting.

Fire Stains in Sterling Silver.—It need hardly be repeated that pure silver does not directly combine with oxygen. The molten metal absorbs or occludes oxygen but expels it again on solidification. Sterling silver contains $7\frac{1}{2}$ per cent of copper which, during annealing processes, is susceptible to oxidation. The oxides formed are tenaciously retained by the silver, and give rise to stains in finished goods which are called fire stains. Annealing the metal in steam would largely, if not entirely, obviate the trouble, but this is seldom resorted to. It has therefore been a practice to finally silver plate sterling silver goods to hide such defects.

These fire stains may be removed without much difficulty. What is wanted is a solvent for the oxide of copper without dissolving the silver.

Rubbing the stains with a solution of potassium cyanide provides one method of removal, and this removes very little silver.

An alternative method is that of a dip of warm nitric acid ($2HNO_3 : 1H_2O$). This removes the copper oxide stain and the film of silver which retained it. It, however, matts the surface, and is not to be recommended for delicate work.

A further dip is :—

Oil of vitriol . . .	8 parts
Nitric acid . . .	1 part

This dip acts slowly, and prior to being put in, the work should be dry or nearly so, otherwise rapid action sets in. If the dip and articles are warmed, the whitening effect is much improved. Rinse in cold water and then in perfectly clean boiling water.

Another satisfactory method is to immerse the goods in warm sulphuric acid (15–20 per cent). This does not produce pitting even with long immersion. After thorough rinsing in cold and hot waters the work may with advantage be passed through a 5 per cent cyanide solution, finally rinsing in cold and hot waters and drying off in sawdust.

In any case the dips accumulate silver and copper, and the recovery of the silver is an easy matter, though outside the scope of the present work.

CHAPTER XV

COLORING OF GOLD

Gold and its Alloys.—Gold occupies a somewh important place in the art of metal coloring. It seldom used in the pure form, being too soft for resistan to ordinary wear and tear. In British coinage 8·34 p cent of copper gave the necessary hardness to gold a also enhanced its color. The usual gold alloys are standardised qualities, represented as "carats" twenty-fourth parts. Thus :—

Fine gold	= 24	carat	= 100% Au
Coinage gold	= 22	,,	= 91·66% Au
	20	,,	= 83·33% Au
	18	,,	= 75% Au
	15	,,	= 62·5% Au
	12	,,	= 50% Au
	9	,,	= 37·5% Au

Such alloys are, when assayed, "hall-marked" at t Assay Office. In the U.S.A., however, no alloy bel 10 carat is marked.

But there is much "gold" which falls outside the alloys. "Rolled gold," for example, is a composite me having a cheap metal base, to which, on one or bo sides, gold—meaning one or other of the above alloys is sweated in various thickness, and the compos metal rolled or drawn down for use. The actual amou

f gold may thus be very small indeed, but that little is at r near the surface.

Properties of Gold.—Pure gold is a heavy and exceedngly malleable metal. Its specific gravity is 19·5 and rdinary gold leaf is an evidence of its malleability. he leaves are green by transmitted light, and this ariation of color can be secured by thin films of the ietal.

A characteristic property of gold is its permanence in ir and its noncorrodibility in many acids. Combined ith its pleasing color these properties make the metal ne of considerable value as a protective and decorative iedium. In color, however, there is room for added alue, and this may be attained by many methods. Much gold" work is merely "gilt" work, and the simple ethod of electro-deposition has already been described some detail in Chapter IX. This is not a very difficult peration but, nevertheless, requires some care and may on be brought under the control of the operator with telligent interest. Variations in the shade of the posited gold are obtained by the presence of other etals in the solution.

Green Color on Gold.—This color is obtained in gildg when the solution contains silver, or silver and lead. iese additions are not large. Silver cyanide (AgCN), as olid, is added to the extent of $\frac{1}{2}$ oz. per gallon of gilding lution. Lead is added as a saturated solution of lead etate in caustic soda. A saturated solution of caustic la is first made and a saturated solution of lead etate is added with stirring until the precipitate first med no longer dissolves. Of the solution formed add l. oz. to 5 gals. of gilding solution.

The solution is used at 160° F., and kept in motion during deposition. It will be gathered that unless we know exactly the proportions in which the metals are deposited we cannot exactly gauge the quantities to be added for replenishing purposes. All additions of lead will be made as the prepared solution. Silver may be added either as silver cyanide or by using an anode of gold and silver, or by placing a small silver anode by the side of the larger gold anode. No exact data can be given, but it may be safely assumed that the needful adjustments can be readily made by intelligent work. The current from a 1–2 volt source will suffice.

The green gold thus obtained is only a color of fair brilliance. It is not improved by either very fine scratch-brushing or with a swansdown mop. The work is rinsed in clean cold and then hot water, and dried out in hot boxwood sawdust. Perfect cleanliness is essential to good results. For a bright finish a bright surface must be used. A satin finish is obtained by preliminary treatment of the surface, either by sandblasting or by scratch brushing and feeding in a little pumice powder.

Subsequent to obtaining the desired green shade a thin coating of lacquer may be applied.

Red Gold (by deposition).—A decidedly reddish color can be imparted to deposited gold by a copper cyanide addition to the gold solution. The copper solution is added a little at a time until the required shade is produced, other working conditions being quite normal to gilding. Other metals, however, should be rigidly excluded. A satisfactory base for the deposition of red gold may be obtained from an old gilding solution with a large excess of cyanide. Used hot, the solution

gives a loose foxy deposit which scratch-brushes down to a satisfactory base.

Changes of shade are quite common to gilding solutions worked under varying conditions. Low temperature and current density produce pale lemon tints. Higher temperature and increased current density improve the shade, while motion of the work makes for a somewhat paler shade. These conditions make uniform working difficult, and the difficulty is further increased when other metals such as silver and copper are added. A watchful eye is necessary, and good judgment is no less essential in order that a balancing up of conditions shall be made to meet the needs of the particular work in hand.

Pink Gold.—This effect is obtained by silverplating the article to be treated. It is then scratch-brushed and a mere film of copper deposited upon it. Gilding is then applied in the ordinary solution, after which parts so required are burnished. After again cleaning the surface free from grease, a very thin film of copper is put on. This film is not scratch-brushed, but is rubbed with a soft cloth and is rinsed in cold and then hot water. When the shade is satisfactory the work is lacquered. A very faint pink shade of lacquer is an advantage.

Ormulu Color on Gold.—Articles for this treatment are first given a fairly stout coating of gold and lightly scratch-brushed. They are then heated to 220° F. and allowed to cool. The coloring composition contains :—

Hæmatite (oxide of iron) .	3 parts by weight	
Alum	1 part	,,
Sea salt	1 ,,	,,

these being made to a paste with vinegar. The paste is applied to parts not to be burnished, and the article

heated until the coloring paste discolors to a blackish shade. It is then plunged, while hot, into cold water, well rinsed, and brushed with vinegar, diluted acetic or nitric acids, afterwards rinsing and drying.

Many alternative mixtures are available. In one, a mixture of potassium nitrate, alum and red oxide of iron is finely ground and worked to a paste with water containing saffron, annatto or other suitable coloring matter. The article is coated with this paste and heated until the paste curls over when touched with the wet finger. More care must be taken if the gold deposit is only a light one. The heated paste is removed by washing. If the paste shows any tendency to sticking it can be removed in weak sulphuric acid (1–10). Too deep a shade can be toned down by brushing with a long bristle brush, striking the work briskly with vertical strokes. On the other hand, the operation of coloring may be repeated if a deeper shade is required.

Red Ormulu requires the following mixture :—

Common salt	1½ parts
Alum	15 ,,
Potassium nitrate	15 ,,
Zinc sulphate	4 ,,
Red ochre	14 ,,
Iron sulphate	½ part

mixed with water containing annatto or madder.

Yellow Ormulu is obtained by using a paste of :—

Potash alum	50 parts
Red ochre	17 ,,
Zinc sulphate	10 ,,
Common salt	3 ,,
Potassium nitrate	20 ,,

For **Dead or Matt Ormulu** use :—

Potassium nitrate	37 parts
Alum	42 ,,
Common salt	12 ,,
Calcium sulphate	4 ,,
Powdered glass	4 ,,

The mixture is finely ground and made to a paste with water.

In each case the paste is applied to the clean work and subsequently heated.

Coloring Alloyed Gold.—Some gold alloys, especially those with copper, have a richer or warmer color than fine gold. The appearance of fine gold can be imparted to such by dissolving out the inferior metal. Two methods are available, *dry coloring* and *wet coloring*.

Dry Coloring.—A powdered mixture of the following composition is prepared :—

Potassium nitrate	4 parts
Common salt	2 ,,
Alum	2 ,,

The mixture is heated in a plumbago pot or crucible until fused. It is stirred with an iron rod and allowed to effervesce. The mixture then settles down to a quiescent state. The work to be treated is suspended in the molten mixture by means of a silver wire and kept in motion for a minute or two. It is then plunged into boiling water faintly acidified with nitric acid. If the shade is not pale enough, the operation may be repeated, and then finally rinsed in hot water containing a little potash and dried out in sawdust. Highly polished work gives the best finish.

Wet Coloring can be safely used for all qualities of gold. The coloring mixture contains :—

Potassium nitrate	24 ozs.
Common salt	12 ,,
Hydrochloric acid	6 fl. ozs.
Water (boiling)	2 ,,

The salts are well ground before adding the liquids. The whole mixture is well stirred and the solids allowed to settle, the work attached to a silver wire being immersed in the mixture for about a minute. Rinse. Add a little water to the coloring mixture and heat to boiling. Re-immerse work. Several such operations may be necessary, further diluting the mixture with each operation. Finally, rinse well in hot water, dry in sawdust. A rich dead gold may be obtained by scratch-brushing with a fine crimped wire brush, using stale beer or vinegar containing a little glue or isinglass as lubricant. The work is, of course, subsequently rinsed and dried.

CHAPTER XVI

COLORING OF ZINC AND NICKEL

Properties of Zinc.—The coloring of zinc should occupy a prominent place in the art of metal coloring, as so many articles of an ornamental character are manufactured from this metal or its alloys.

Normally the metal is fairly stable under atmospheric conditions. In an acid atmosphere it rapidly deteriorates. The action of such acids, even in very dilute form, as sulphuric, hydrochloric and nitric, give clear indication of this instability. The zinc compounds formed with these acids are readily soluble, and, being washed away, leave a clean zinc surface free for further attack. In an acid-free atmosphere, however, zinc may still be subject to attack by carbonic acid gas, oxygen and moisture. Under these circumstances, however, thin films of insoluble compounds, such as oxide and carbonate, are formed. These adhere to the surface of the metal and offer protection. It is partly on these grounds that the process of galvanising is so largely resorted to in the protection of iron and steel, though there are other reasons of an electro-chemical character which come into play.

Again, a slight knowledge of the properties of zinc compounds reveals the almost entire absence of color in them. All the usual zinc compounds are white, and any

process of coloring zinc will thus necessitate the production of a film of a colored compound of some other metal. This will be traced in the operations now to be described. Of these colored compounds those of copper are most prominent, and these are obtained by treating the zinc with some type of copper solution. It will be recalled that zinc readily turns out copper from solutions of many of its salts.

In the case of copper sulphate :—

$$Zn + CuSO_4 = Cu + ZnSO_4$$

and even the much more stable double cyanide compound is susceptible to a similar change when :—

$$Zn + 2CuCN{\cdot}KCN = Zn(CN)_2{\cdot}2KCN + 2Cu$$

Reference is made in Chapter IV to the nature of such deposits.

Brown Shades on Zinc.

Solution I :—

Copper nitrate . .	2 lbs.	200 grms.
Water	1 gal.	1 litre

The solution is worked 65° F. and a dark brown to black shade is easily obtained which, after rinsing in cold and hot water, is dried off in sawdust, lightly but briskly rubbed with a soft cloth and lacquered with a black-tinted lacquer. The brown color is due to cuprous oxide (Cu_2O).

Solution II :—

Copper sulphate . .	6 ozs.	38 grms.
Sodium carbonate (cryst.)	4 lbs.	400 ,,
Sugar	9 ozs.	56 ,,
Water	1 gal.	1 litre

Ordinarily sodium carbonate and copper sulphate might be expected to give a green precipitate of basic copper carbonate. In the presence of organic substances, such as sugar, cream of tartar, etc., blue soluble compounds are formed. Such solutions were first used for coppering on iron and zinc before the introduction of the cyanide solution.

The solution is applied by painting and the work allowed to dry. It is then lightly brushed, heated on a hot plate and finished by brushing and lacquering. This treatment imparts a good brown shade.

Iridescent Colors.

Solution I :—

Copper tartrate . .	1½ lbs.	150 grms.
Caustic soda . . .	2 ,,	200 ,,
Water	1 gal.	1 litre

This is another of the blue organo-metallic compounds of copper. The solution is used at 110° F. and on zinc a succession of shades is produced, viz., coppery shade, yellow, light brown, crimson, blue, purple, pale purple, light green and finishing with light crimson. These shades are beautiful but not uniform. They give an iridescent effect. The cold solution works slowly, but is easily controlled. The warm solution works more rapidly, but is more different to control. Such a solution is open to wide variation of composition, thus :—

Solution II :—

Copper sulphate . .	½ lb.	50 grms.
Cream of tartar ($KHC_4H_4O_6$)	½ ,,	50 ,,
Sodium carbonate . .	1½ lbs.	150 ,,
Water	1 gal.	1 litre

The effects of this solution are similar to those of the previous solution, except that they are somewhat denser and less brilliant. Every conceivable shade is, however, obtainable, due to varying thicknesses of the films of copper and cuprous oxide deposited on the zinc. It is, as usual, important that the work should be as chemically clean as for electroplating, and that the shortest time possible elapses between the cleaning of the metal and its immersion in the coloring solution. The usual precautions in finishing also need emphasis.

Grey Color on Zinc.—Other metallic solutions which are easily decomposed by zinc with the deposition of the metal include those of arsenic, of use in obtaining a grey color.

Solution :—

Arsenious acid . .	6 ozs.	37·5 grms.
Potassium cyanide . .	10 ,,	62·5 ,,
Sodium phosphate . .	2 ,,	12·5 ,,
Water	1 gal.	1 litre

From an acid solution of arsenic, such as that obtained by dissolving arsenious oxide in hydrochloric acid, arsenic is precipitated rapidly by means of zinc, when :—

$$3Zn + 2AsCl_3 = 3ZnCl_2 + 2As$$

A dark, loose, nonadherent deposit is obtained. From the cyanide solution, however, the action is much slower, leading to a thinner but more compact and adherent film. The solution may be used warm or cold and the work immersed in it, or the solution brushed over the work. After rinsing and drying, finishing may be effected either by lacquering, or with a wax brush to give an opaque or egg-shell finish.

Ebony-black on Zinc.

Solution :—

Copper nitrate . .	1 oz.	6·25 grms.
Ammonium chloride .	1 ,,	6·25 ,,
Copper chloride . .	1 ,,	6·25 ,,
Hydrochloric acid . .	1 fl. oz.	6·25 cc.
Water	1 gal.	1 litre

The solution is readily made, but the shade may require a little patience. The cleaned work is immersed in the solution or the latter applied by brushing. Dry on a hot plate at not more than 100° F. Slow drying is preferable to quick drying. When quite dry apply a vigorous bristle brushing, followed by heating in a stove to 160° F. for about 15 minutes. Cool and dry scratch-brush. Lacquer with transparent or black-tinted lacquer and stove at 70° F. for about 15 minutes. The work must not be handled while warm. When cold the surface is hard and durable. If a dead black surface is required the work may be sandblasted before lacquering or waxing.

Nickel and its Compounds.—The coloring of nickel is by no means so common an operation as with several other metals which have already been dealt with. The application of nickel in protective and decorative work is most usually confined to the production of highly polished electro-deposits so common on cycle, motor, instrument and domestic fittings and appliances. The coloring of such deposits is an uncommon operation.

These highly polished surfaces of electro-deposited nickel are marked by their great permanence in air, again doubtless due to the formation of a comparatively thin film of protective oxide. Such an invisible film is readily

formed. Under different circumstances it works very advantageously and also quite the reverse. An unhappy effect of this film formation is the tendency to stripping shown by nickel-plating when, during the process, the work has been removed from the bath for the purposes of inspection. Every plater knows that this is a procedure which is not to be recommended. On the same principle it has been loosely affirmed that nickel cannot be plated on to nickel. This, of course, is an absurd statement. What is rather meant is that a new deposit of nickel is nonadherent to an old deposit, on account of this film of oxide which defies mechanical means for its removal.

Again, a number of nickel compounds have distinctive colors. Of the compounds which are insoluble in water, and which might therefore form color films, there are the green oxide (NiO), black oxide (Ni_2O_3) and green carbonates and hydroxide. Nickel sulphide is black and offers other possibilities of shades according to the thickness of film produced. These methods are, however, seldom resorted to. Occasionally thin films of copper or brass are applied to nickel and subsequently colored. The most common form of decoration, however, is what is called " black nickelling."

Black Nickel.—The term is a little vague and is often used for results which are in no way due to nickel. As ordinarily deposited, nickel is white. The presence of impurities in the nickel bath gives rise to a dark deposit. The problem is the addition of such constituents as will yield a uniform black deposit which may satisfactorily meet the desire for a change from the pure white deposit.

Such results may be obtained over quite a wide range of solutions. Varying with the solution is the com-

position of the deposit. As will be seen below, some solutions contain large proportions of arsenic compounds. From such, the deposit is mainly one of arsenic, and thus does not merit the name of black nickel, the only association with nickel being the fact that some nickel salts are used in the solution and the deposit, too, contains a small proportion of this metal. Such deposits are dark grey to bluish black.

Quite another type of compounded solution contains nickel salts, zinc sulphate and a sulphur compound, usually sodium sulphocyanide (NaCNS), potassium sulphocyanide (KCNS) or ammonium sulphocyanide (NH_4CNS). Analysis of the deposit goes to show that it contains nickel, nickel sulphide, zinc and organic matter of an indefinite type. But the deposit is a dead black and is in no small demand.

Somewhat fanciful solutions and methods are often recommended from which to obtain such results. As before stated, every constituent in a plating or coloring should justify its presence by some definite purpose, and the simpler the composition, the more likely is the solution to possess permanence in producing satisfactorily uniform results. Complicated "formulas" are undesirable. They, too, easily go astray and then defy methods of rectification.

Black Nickel Solution.—The following solution will be found to give good results :—

Nickel ammonium sulphate	10 ozs.	62·5 grms.
Zinc sulphate . .	1·25 ,,	7·8 ,,
Sodium sulphocyanide .	2·5 ,,	15·6 ,,
Water	1 gal.	1 litre

This solution is used as a depositing solution. The work

to be black nickelled is made cathode, and anodes of nickel are used. Rolled nickel anodes are to be preferred. These usually give rise to acidity, and this acidity may best be neutralised by keeping a small quantity of zinc carbonate suspended in the solution. This is a more satisfactory method than periodically attempting to neutralise the acid with ammonia. The personal element of the operator will find room for exercise. The P.D. between anode and cathode will be between 2 and 4 volts. The figure varies with quite a number of conditions of local value, and the operator will do well to work the solution in the spirit of research to find the best conditions and henceforth to keep them. Preliminary cleaning of the strictest type must be adhered to or success will not follow. All necessary polishing should be done first. Scratches cannot be eliminated afterwards. With the usual thickness of deposits, scratches are not filled up, and subsequent polishing to remove them will result in the metal deposited being worn through. To remove such scratches "blinding" is sometimes resorted to. This consists of polishing lengthwise with the scratch with lime and tallow. This brightens the scratch so that it is less conspicuous. But this is done at the expense of the plated metal, and only a very substantial deposit will stand it.

Maintenance of Solution.—It may be a comparatively easy matter to obtain a satisfactory black nickel deposit. The problem rather is to maintain the solution of such composition as will guarantee the continuance of the good result first obtained. The reactions are complicated. If the zinc sulphate content is high the deposit will become greyish. Consider the changes. In the deposit nickel comes from the solution and there from the anode.

With a nickel anode a continuous supply of nickel is forthcoming without, however, any guarantee as to its being in the exact amount required.

Zinc in the deposit comes from the solution, which will therefore require replenishing with zinc sulphate. The sulphur and organic matter in the deposit are derived from the sodium or potassium sulphocyanide. This substance must therefore be added at intervals. Nothing but an exact analysis of both solution and deposit would serve to indicate the relative qualities of essential materials present. This, however, is outside the range of practical work and only approximate tests are available. Cast nickel anodes would dissolve too freely, and the solution would become enriched in nickel as the deposit may only contain 60 per cent of this metal. Zinc anodes would at once lead to an excess of zinc in the solution and deposit. The zinc finds its way into the deposit from the solution. It is originally introduced into the solution as zinc sulphate, but is subsequently added as zinc carbonate, which, stirred into the solution, is taken up by the free acid purposely formed in keeping down the solubility of the nickel anode. Finally, sulphocyanide must be added from time to time.

It has been suggested that the current conditions would be best explored by the operator. It will be found that about 1 ampere per sq. ft. will suffice.

The Cyanide Solution.—Many different formulas have been given for such solutions. Usually they have been too complex to be at all satisfactory. A feature of these solutions is a large proportion of arsenic compounds, and arsenic enters largely into the deposit which is in color bluish black or grey.

One *solution* recommended is :—

Double nickel salts	8 ozs.	50 grms.
Zinc sulphate	$\frac{2}{3}$ oz.	4 ,,
Ammonium carbonate	6·5 ozs.	40 ,,
Arsenious oxide	1 oz.	6 ,,
Sodium hydroxide	1·7 ,,	10 ,,
Sodium cyanide Potassium cyanide	8 ozs.	50 ,,
Water	1 gal.	1 litre

Such a solution probably contains, when made, double cyanide of nickel and potassium [$Ni(CN)_2 2KCN$], the similar compound of zinc, and sodium arsenite (Na_3AsO_3). Nickel anodes are used. The function of the zinc sulphate is not apparent, and in any case the solution is very difficult to maintain in good working condition. Under these circumstances it is not one which can with confidence be recommended.

Bluish Black.

Solution :—

Arsenious oxide	2 lbs.	200 grms.
Hydrochloric acid	1 gal.	1 litre

The arsenic compound dissolves readily on warming, but the fumes must on no account be inhaled. To the warm solution add :—

Nickel sulphate	4 ozs.	25 grms.
Copper sulphate	1 oz.	6 ,,
Hydrochloric acid	1 gal.	1 litre

A cast nickel anode with a low current density must be used. The deposit consists mainly of arsenic, and this will indicate the direction in which the composition of the solution must be maintained.

Having obtained the black color, finish off with cold and hot waters, sawdust and a soft swansdown mop with rouge or Sheffield lime.

Golden Tint on Nickel.—This is obtained by applying a very thin film of copper (from the cyanide bath) on to a deposit of nickel. So thin must the film be that, on scratch-brushing, the surface should appear as nickel with only a slight sheen.

Coloring Solution :—

Ammonium sulphide .	$\frac{1}{4}$ oz.	1–2 c.c.
Water	1 gal.	1 litre

The work is passed momentarily through this solution, rinsed and dried off and, after wiping with a soft cloth, is lacquered with a pale gold lacquer.

A paler shade may be obtained directly on the nickel without the copper, the solution being used warm.

Nickel goods may be colored in many shades by first applying a substantial coating of copper or brass by electro-deposition and then applying the usual coloring media as already outlined for these metals.

Gold-bronze Tint on Nickel.

Solution :—

Barium sulphide . .	$\frac{3}{4}$ oz.	4·5 grms.
Water	1 gal.	1 litre

The solution is used at 100–160° F., the shade varying with the temperature. The same solution at one-half to one-third of the above strength and used cold produc a coinage-bronze color.

A pleasing effect may be produced by beating the surface with a bristle brush charged with pumice powder

or silver sand according to the fineness of the finish required.

Chandelier Grey Nickel Finish.

Solution :—

White arsenic . .	5 ozs.	32 grms.
Caustic soda (98 per cent)	12 ,,	75 ,,
Water	1 gal.	1 litre

A small amount of potassium cyanide (say, ½ oz. per gal.) may be added. The solution is used as for deposition purposes, with a brass or steel anode and a P.D. of 3–4 volts. This treatment for 5 minutes will serve to give the desired effect.

Novelty Grey Finish.—This is obtained solely by the deposition of nickel on all classes of metals. These are first suitably coppered, the base metals first passing through the cyanide bath. The acid bath preferably contains an addition of 3 ozs. of common salt per gal. Deposition for 15 minutes at 15–20 amperes per sq. ft. should suffice. Subsequent nickelling is effected in a solution such as that shown on page 119, to which common salt may be added even to saturation. Five minutes' deposition will here suffice.

Several effects are possible. A completely matt result will be produced by nickel-plating on the thoroughly rinsed matt surface from the acid copper bath. Alternatively, low lights may be left dead with the high lights burnished, the operation being done with care to avoid interference with the dead surface on the low lights.

After nickel-plating, the work is rinsed through cold and then hot water and dried off in clean boxwood sawdust.

CHAPTER XVII

COLORING OF IRON AND TIN

It frequently becomes necessary to obtain colored effects on iron and steel in order to obtain harmony with other metal furniture. For this purpose both direct and indirect methods are available, indirect methods being those in which other colorable metals are first deposited upon the iron.

Tempering Colors.—The correct working properties of many tool steels are acquired by first hardening the steel and then subjecting it to a thermal treatment in which it is raised to certain definite temperatures. These temperatures are computed with a considerable degree of accuracy by the definite colors of the oxide films which form on the surface during heating. The temperatures and shades are :—

220° C. . .	pale yellow
230° C. . .	straw-yellow
255° C. . .	brownish yellow
265° C. . .	purple-yellow
277° C. . .	purple
288° C. . .	light blue
293° C. . .	dark blue
316° C. . .	blackish blue

The toolmaker obtains these colors merely as indications of temperature, but they are all fairly permanent in a

dry atmosphere and may be rendered more so by a coating of transparent lacquer.

Blue Color on Iron.—Upon the iron is first obtained a highly polished surface, finishing with a dry mop and dry Sheffield lime. The work is now freed from grease and dirt, and passed through a strong vinegar and allowed to drain for a few minutes. The surface is then wiped over with hydrochloric acid, the acid being spread very uniformly and then allowed to dry. It is then heated on a sandbath, when a satisfactory blue shade appears.

Various Colors may be produced on polished iron or steel in a solution already described on page 160. This consists of :—

Lead acetate . . .	1½ ozs.	10 grms.
Sodium thiosulphate .	1½ ,,	10 ,,
Water	1 gal.	1 litre

With the mixture at 200° F. a succession of colors results. The successive colors are light brown, dark brown, purple, light blue, steel grey and finally black. These colors are due to films of lead sulphide. After rinsing and drying, the colors may be rendered still more permanent by the application of a transparent lacquer.

"Browning" by Bronzing Salt.—Make a paste of antimony chloride (butter of antimony, $SbCl_3$) and olive oil of about the same consistency as cream. The iron surface is cleaned, dried and warmed and the paste applied. On standing, the iron acquires a brown color, but the effect is hastened by the addition of a little nitric acid to the mixture.

A somewhat more complicated, but nevertheless very effective, method is as follows :—

Solution I :—

Copper sulphate . .	8 ozs.	50 grms.
Ferric chloride . .	2 ,,	12½ ,,
Nitric acid . . .	2 fl. ozs.	12½ c.c.
Spirits of nitre . .	1 fl. oz.	6 ,,
Alcohol	2 fl. ozs.	12½ ,,
Water	1 gal.	1 litre

or *Solution II :—*

Copper sulphate . .	8 ozs.	50 grms.
Spirits of nitre . .	8 fl. ozs.	50 c.c.
Water	1 gal.	1 litre

These solutions are evenly applied to the carefully cleaned iron or steel and allowed to dry and to stand for 24 hours. The following mechanical operations are then carried out in order :—brushing with an old fine wire steel scratch brush, polishing with a piece of hard wood, coating with shellac varnish, drying hard, further polishing with hard wood and finishing by briskly rubbing with a velvet pad.

Buchner's Method for Gun Barrels.

Solution :—

Ferric chloride . .	32 ozs.	200 grms.
Antimony chloride . .	¾ oz.	4 ,,
Gallic acid . . .	¾ ,,	4 ,,
Water	1 gal.	1 litre

This solution is used hot, when different shades appear in the following order : (1) pale blue, (2) purple, (3) plumbago-grey. The work is finished as given above.

Grey Color on Iron.—The work is first cleaned and coppered in the cyanide bath, and then treated in :—

Ammonium sulphide .	24 fl. ozs.	150 c.c.
Water	1 gal.	1 litre

Several immersions may be necessary in order to obtain a uniform and dark color. The work is now rinsed, wet scratch-brushed, dried quickly and lacquered.

Black on Iron.

Solution :—

Sodium thiosulphate .	4 ozs.	25 grms.
Water	1 gal.	1 litre

The solution is used at 200° F. and several successive immersions may be required in order to obtain the necessary density of color. This is followed by the usual finishing.

Frosting Iron Buckles.—An iron plating solution is required for this purpose, and several are available from which good results are easily assured.

Solution : Take a saturated solution of ammonium chloride (NH_4Cl) and pass an electric current through it from a large anode and on to a smaller cathode. Soft charcoal iron is the best metal for the anode. About 6 volts at the bath terminals will be found suitable. Iron is dissolved from the anode into the solution which then contains ferrous chloride ($FeCl_2$). As the content of iron increases in the bath, the metal will begin to be deposited, and when this deposit is regarded as satisfactory the cleaned and scoured buckles may be put in on the cathode bar to receive a deposit of iron for about 20 minutes. If the operator is versed in the simple principles of electro-deposition, this will constitute a simple task. Even to the

uninitiated it should not prove difficult. Deposition for 20 minutes suffices, after which quick rinsing in cold and hot water and a quick drying out in sawdust ensures freedom from stains. Transparent lacquer may then be applied, or the work rubbed up with an oily cloth.

Rust-resisting Processes.—Many and varied are the methods which have from time to time been proposed as rust preventatives. Many of these aim at the production of a continuous film of oxide on the surface of the iron, and must be regarded as of considerable success.

The Parker Process.

Solution :—

Phosphoric acid (H_3PO_4) .	4 ozs.	25 grms.
Manganese dioxide (MnO_2)	$\frac{1}{4}$ oz.	$1\frac{1}{2}$,,
Water	1 gal.	1 litre

The article is boiled in this solution for 2–4 hours in an iron tank. Cast iron in a finely powdered state may be substituted for the manganese dioxide. When coated with a dark grey deposit, the work is rinsed in cold then in hot water and dried in sawdust. Particles of sawdust are then removed by brushing and the work heated on a hot plate, until water dropped upon it is instantly thrown off. At this temperature the work is immersed in linseed oil, removed, drained and gently heated to dryness. Thus runs the Parker formula. The following method can, however, be much more confidently recommended as the result of the long experience of one of the authors.

Another Method.

Solution :—

Calcium hydrophosphate ($CaHPO_4$) . . .	$1\frac{1}{2}$ lbs.	150 grms.
Water	1 gal.	1 litre

Boil the work in this solution and, when a slaty color is attained, remove, rinse in cold and hot waters and dry out in sawdust. Then immerse in a heavy oil which is kept at about 212° F. for about 1 hour. For light goods a shorter period of immersion will suffice. Finally remove, drain and finish as before directed.

Iron and steel goods will withstand the effects of the atmosphere for some time after being made hot and immersing in linseed oil at a temperature of 600° F., draining off superfluous oil and drying on a hot plate. Old goods should be ground bright, and any rust removed before being put through the process.

Yet another method consists in boiling the work in the following

Solution :—

Hydrophosphate of iron . . .	5 lbs.
Water	1 gal.

until a dark grey color appears and then rinsing, drying and finishing off with oil as previously indicated.

Treatment of Nuts and Bolts.—These and similar small articles may be temporarily protected by first polishing bright with a bob treated with 120 emery, then heating to a "black heat" and plunging warm into heavy engine oil such as would ordinarily be used in a gas engine cylinder. After draining, the oil is dried off with heat. A repetition of the process adds to the permanence of the result.

A Good Method of Protection.—Where a good heat can be applied, iron articles can be very satisfactorily treated by coppering first in the alkaline bath, scratch-brushing and then well plating in a zinc cyanide solution.

After drying, the articles are heated up to 600° F. in an iron or copper pot and immersed in a heavy oil, afterwards draining and drying. It is of advantage to cool the article after heating and to scratch brush with a coarse wire brush prior to the oil immersion. Alternatively to oil treatment, the work may be lacquered with a black shade of lacquer and the lacquer gently burned off while still wet. Bicycle brake fittings done in this manner will resist rust for quite a long time.

Direct Coloring of Steel.—A pleasing and useful effect can be obtained on steel goods by the following solutions :—

Solution A :—

Copper sulphate . .	3 ozs.	20 grms.
Hydrochloric acid . .	2 fl. ozs.	13 c.c.
Water	1 gal.	1 litre

Solution B :—

Arsenious oxide . .	2¼ lbs.	225 grms.
Copper sulphate . .	1 oz.	6 ,,
Hydrochloric acid . .	1 gal.	1 litre

Solution B must be warmed in the course of preparation, and the fumes which are highly poisonous must be avoided. The arsenious oxide should entirely dissolve.

The steel work is carefully cleaned as for plating and passed through A, maintaining motion until a copper color is acquired. Without rinsing, the work is passed to Solution B, previously stirred, and again kept in motion until a black smoky shade appears. Rinse well in boiling water and dry in an oven or over a hot plate. Scratch-brush with a steel wire brush. The effect may be darkened by passing a second time through B and finishing by lacquering.

Metallochromes.—A very interesting decorative effect was obtained by Nobili in 1826 and hence came to be called Nobili's rings. As has been pointed out, many of the color effects are due to the splitting up of light—giving a rainbow effect—as it passes through very thin films of deposits. If a film can be deposited in a circular form with the greatest thickness at the centre, the uniformly decreasing thickness will produce a succession of these small rainbows. They may also be produced by lightly pressing a slightly convex lens against a flat glass surface. The physicist then calls the effect "Newton's rings."

From the metal-coloring point of view the film may be built up of lead peroxide (PbO_2). In many lead-plating solutions, particularly those which are alkaline, there is a tendency to the formation of lead peroxide at the anode. If the cathode is a wire fixed to present only a point opposite to the anode, the desired effect may be obtained. The effects are best produced on polished steel or nickel. Several solutions are available.

Solution I: A saturated solution of lead acetate. This should be preferably made in distilled water. If only ordinary water is obtainable this should be boiled for half an hour, cooled and filtered to remove the deposit which frequently is chalk. The water is now saturated with lead acetate. The amount required will be about 3 lbs. per gallon (300 grms. per litre). A turbid solution results, due to partial decomposition of the lead acetate. The turbidity is removed by filtering. The solution is best used on a flat dish—porcelain or enamelled. A piece of polished steel is laid at the bottom of the dish and by a suitable wire connection made anode. The clear solution

is poured over and a copper wire is introduced as cathode. Lead is deposited on the wire as a loose mass, but this can be readily wiped away. A current from a 4 volt circuit will be found suitable and the rings are soon produced. Alternatively, the wire may be bent into any desired shape—circular, square or triangular—and the rainbow rings will follow a like form on the anode. Sharper effects are obtained when the wire is nearer to the anode. When a satisfactory effect is obtained the work may be dried off and lightly rubbed with a soft pad of cloth.

Solution II :—

Caustic potash . .	1 lb.	100 grms.
Litharge . . .	10 ozs.	62·5 ,,
Water	1 gal.	1 litre

These materials are boiled together and stirred. The bulk of the litharge is dissolved thus :—

$$2KOH + PbO = K_2PbO_2 + H_2O$$

The soluble lead compound is potassium plumbite. The solution is cooled. Excess of litharge being very heavy may be allowed to settle and the clear liquid poured off. Filtering is not necessary. For use, this solution is diluted with its own bulk of water, and the used solution may be strengthened from time to time by additions of the strong solution. The mode of operation is the same as for Solution No. 1.

Nickel-plated surfaces of high finish can be treated with excellent results. Toys may be made to look very attractive. Variations of design may be made by cutting designs in sheets of nonconductive materials and laying these over the face of a copper sheet used as cathode.

Other possibilities will soon suggest themselves to the operator.

Coloring of Tin.—Tin and its Properties.—Tin as a metal is fairly permanent in air, dry or moist. Further, most of its compounds are white, including its two oxides, SnO and SnO_2. Of its two sulphides, stannous sulphide (SnS) is, when obtained by precipitation, brown, while stannic sulphide (SnS_2) is yellow. The metal hardly lends itself to direct coloring but, after electro-deposition of other metals upon it, offers all the usual possibilities. The few available direct methods cannot be regarded as eminently satisfactory.

Brown Color on Tin.

Solution :—

Copper sulphate . .	10 ozs.	62·5 grms.
Ferrous sulphate . .	10 ,,	62·5 ,,
Water	1 gal.	1 litre

The suitably cleaned tin article is treated in this solution at a temperature of 160° F. and acquires a brown shade. After rinsing and drying it is polished with a waxed brush and thus assumes a fairly good bronze color.

Moiré Métallique.—This term is applied to a beautiful crystalline surface which may be induced on tin plate—by which is meant iron or steel coated with tin. The tin plate is first heated until the tin shows signs of melting at the edges and then, while hot, is plunged into the following acid solution :—

Nitric acid . . .	1½ fl. ozs.	9 c.c.
Sulphuric acid . .	16 ,,	100 ,,
Water . . .	1 gal.	1 litre

A somewhat coarser structure is obtained if the acid solution is used at a temperature of about 100° F. After rinsing and drying out in sawdust, the sawdust is completely removed by brushing and the work lacquered, using a colorless lacquer. Colored effects can be obtained by the use of tinted lacquers. Such tinted lacquers are prepared by dissolving aniline dyes in the thinner, which is then added in the required amount to give the necessary color. An excess of thinner will, however, make the lacquer flow too readily. There is thus some scope for colored effects by this process.

CHAPTER XVIII

THE COLORING OF ALUMINIUM

Introduction.—The deposition of metals on aluminium is a subject fruitful of inventive effort, and, incidentally, much disappointment. The files at the Patent Office carry more than a fair proportion of suggestions which have from time to time been made with a view to overcoming this eternal problem. The cause of the difficulty is common to the soldering and welding of the metal. All aluminium carries a thin and tenaciously adherent film of oxide. This renders excellent protective service, but it also offers an excellent opposition to the adhesion of superimposed metals, whether by plating, soldering or welding. Big things have from time to time been promised, to be followed by equally big disappointments.

Pickling Aluminium.—In order to free aluminium from grease, oxide and other foreign substances, the German aluminium industry recommended a 10 per cent solution of caustic soda saturated with common salt. A 15–20 seconds' immersion of the metal is followed by rinsing and brushing and a further dip of 30 seconds given. The metal is then washed in running water and dried in sawdust. A matt silver effect is thus obtained. If only a good polished silver effect is required, dipping in dilute caustic soda will suffice, followed by thorough rinsing and drying.

The Plating of Aluminium. It is about sixteen years

since one of the authors was approached by a firm of telephone manufacturers to nickel-plate aluminium telephones. A refusal to undertake the work could not be taken as the order for the nickel-plated goods had been accepted, some of which were required for steamships and yachts. The nickel-plating was therefore undertaken on the understanding that not more than eighteen months' service could be expected or guaranteed. The work was done, and in less than this stipulated time the fittings had to be removed and were not replaced by similar work. Sea air has a most detrimental effect on aluminium. In the case of these fittings, the nickel-plate began to blister, especially where handled, and soon peeled.

The at first apparent success of the plating brought forth many enquiries and other types of aluminium ware were tried. The writer has before him a candlestick stem which was nickel-plated sixteen years ago. The plating is not perfect now, minor imperfections, consisting of pimples of the size of a pin-head, being obvious. The cost of the work was, however, prohibitive.

Method.—The following method was used. The articles were polished in the usual manner, limed and dried off with Sheffield lime and passed to the plating shop, where they were subjected to a scouring with Sheffield lime and pumice powder with a 25 per cent alum solution. The scouring was very quickly performed and the work rinsed in alum water and passed into a 10 per cent sulphuric acid, then into the acid copper bath of the best possible type. No other goods were allowed in the solution at the same time. The articles were struck at once and the deposition allowed to proceed for a time to ensure a satisfactory thickness. The deposits were

scratch-brushed with clean water and a clean brush. The scouring process with lime was then repeated and the work passed through to the nickel bath, struck at once and then plated slowly for about an hour or less. Again, no other metals must be in the bath at the same time. The work was then finished as with ordinary nickel-plate.

Direct plating of nickel on the aluminium, without the intermediate coppering, may be done, but it is much more difficult to guarantee an adhesive deposit.

Several other points of importance attach to the plating of aluminium goods. Such work must not be potashed in the same way as copper, brass and iron. Aluminium dissolves as freely in potash as in acid, thus :—

$$2Al + 6KOH = 2K_3AlO_3 + 3H_2$$

The same reaction occurs with caustic soda :—

$$2Al + 6NaOH = 2Na_3AlO_3 + 3H_2$$

Sodium aluminate (Na_3AlO_3) may appear an unimportant compound, but as a point of interest it may, in passing, be said that every ounce of aluminium in the course of manufacture goes through this form. The careless suspension of aluminium in potash has doubtless led to many a mystery of disappearing articles or parts.

This, however, does not entirely prohibit the use of potash with aluminium, but the application should only be made by lightly scouring with a mop, which should be effective if the articles have been properly dried off with lime.

Alternative Method.—An alternative treatment of aluminium previous to plating consists in first cleaning the metal in potash and then scouring with milk of lime. After rinsing, the aluminium is transferred to a weak

potassium cyanide solution of about ·2 per cent. After again rinsing, it is passed into a solution of ferric chloride ($FeCl_3$) and allowed to remain until it becomes distinctly crystalline. After further rinsing it is transferred to the plating bath, and with this treatment it may be even nickel-plated direct.

Matt Aluminium.—Picture frames and similar goods of aluminium may be given a finish somewhat like matt silver in a solution of caustic soda. This substance is thoroughly dissolved to the extent of 5 per cent and the article laid in the solution with the finish side uppermost. The solution soon attacks the metal and froths up owing to the evolution of hydrogen. The work is then removed, rinsed in clean cold water and dried off in clean hot boxwood sawdust, using a soft dusting brush to remove the last traces of sawdust.

Inconveniently shaped work may be treated by brushing with the solution, and a pleasing contrast may be obtained by treating some parts with the alkali while others are left burnished. A little experience is necessary to obtain a first-class effect. Possible defects are streaks and unsightly spots. The time of immersion and strength of solution may be varied by any intelligent operator. The preliminary removal of all greasy material is essential.

Aluminium Pickle.—For the pickling of aluminium and its alloys, some special treatment is necessary. The metal is not so readily amenable to acid treatment as are most metals.

Solution I :—

Caustic soda . . .	1 lb.	100 grms.
Water	1 gal.	1 litre

This is used at 165° F., and for a few seconds only, as a means of removing grease. The work is then rinsed in clean water and passed into

Solution II, which contains:—

Nitric acid . . .	60	parts by weight
Water	100	,, ,,

As it leaves the alkali solution the work is coated with white oxide (Al_2O_3). This is instantly removed by the nitric acid dip, leaving the surface of the metal clean and white. The work is now rinsed in clean cold and then hot water, and dried in sawdust. If, for durability, lacquering is to be applied, only a clear water-white lacquer should be used. This remark applies to all aluminium goods.

Brown on Aluminium.—A brown color is said to be obtained on aluminium by an electrolytic method. The solution used is:—

Ammonium molybdate . . .	20 grms.
Strong ammonia solution (·880)	20–25 c.c.
Water	2 litres

The solution is treated with sulphuretted hydrogen by passing the gas through until it assumes a deep red color. It is heated to 140° F. and a current of 1 ampere per sq. dm. (9·2 amperes per sq. ft.) passed on to the aluminium made cathode. A zinc anode is used and the P.D. required is 3–4 volts.

CHAPTER XIX

VARIOUS PROCESSES

Redecoration.—It may sometimes happen that the metal colorer will be asked to redecorate articles of an ornamental character, such as those which are often seen in India, China and Japan. Goods of this class, after years of wear, lose their beauty and require the artist's service to again bring out some, if not all, of their original charm. Usually there is enough of the old coloring left to serve as a guide.

To deal with this matter the best way is to grind the colors in turpentine and add sufficient copal varnish to obtain the correct consistency for applying with a brush.

A piece of sheet zinc may be used for testing the result of mixing the necessary colors, in order to produce the right shade. In some types of this ware, there may be three or even more different shades to bring out, and some of these in very small patches. The nature of the figure may vary widely, from a Japanese warrior in armour to a highly colored Indian god; but whatever the job may be, the colorer with ingredients to hand and a little of the artistic temperament, should be able to turn out a result almost, if not quite, equal to the original.

The application of the different shades of color so as to

harmonise, requires some skill on the part of the manipulator, especially if originality is to be displayed, though less skill will be necessary in merely copying previous coloring. The task must not be considered a simple one, especially if the result is to do the workman credit.

Of the colors met on this class of work, red, green and gold are common. They frequently intermingle and shade off into each other with a softness that is beautiful. If the ground-work is green and red has to blend with it, the red must fade off to a pale red, while gold should fade off into black or white, according to the original coloring. There should be, as a rule, no abruptness between adjacent colors. In a few cases in which an abruptness occurs, the color at the dividing-line should be of a darker shade.

After having faithfully reproduced the colors of the figure, it is next placed in an enamelling stove at a temperature not exceeding 100° F. for about half an hour, and not handled again until it is quite dry and hard.

Bronze Powders.—Bronze powders are examples of very finely divided metals and alloys of which a selection may be made to give a fair range of color. These metals and alloys are very malleable, and can be successfully reduced to very thin films which are further ground down in some convenient medium to prevent dusting. This medium is then washed out and the powder dried.

The powders are applied to an article by first coating it with a shaded varnish or slow-drying lacquer. When this is nearly dry, or in what is called a "tacky" state, the bronze powder is dusted on with either a soft brush

or a piece of wash-leather. It is then very lightly and smoothly rubbed and put in an oven to dry and harden. It may afterwards be lacquered with a clear lacquer.

The process is applicable to plaster and wood articles, but in the case of wood it is not advisable to use heat for drying.

Much of this class of work is now done by spraying, and beautiful shadings are both possible and obtained by this method. Indeed, articles of wood pulp have been most artistically decorated in this manner by Mr. E. H. Bonney, who is a specialist in this class of work.

Plating Non-metallic Surfaces.—The successful coloring of many non-metallic materials such as wood, plaster, china, etc., demands in many cases that these materials must first be coated with a metal. This metal is applied by electro-deposition, but before this can be effected it is essential that the surface shall be conductive to the electric current, apart from which no deposit can possibly be obtained. This process of rendering the surface conductive is generally termed metallising, though, as will be seen, the films produced are not always of metals. Graphite and a number of sulphides are useful for this purpose.

The process aims at imparting to the surface a thin film which must be absolutely continuous and adherent. Such treated surfaces will receive in a plating solution a deposit which may be of any desired thickness, after which, with some modifications, the ordinary metal-coloring processes may be applied.

Treatment of Plaster.—The article, probably a plaster figure, is first *very gently* warmed in order to expel any moisture from the pores. It is then immersed in boiled

linseed oil for about half an hour, after which it is removed and allowed to drain. When the draining is complete, the article is transferred to an oven and kept at a temperature of about 160° F. until the oil dries and hardens. The time will depend upon the size of the article. Small articles will dry off quickly. The surface is now examined. There must be a complete and continuous film of the hardened oil. Failing this, the plating solution into which the plaster figure is subsequently put will find its way into the porous plaster, and by crystallisation will bring about the disintegration of the figure. The oil treatment is to render the plaster completely impervious to liquids, and in order to attain this it may be necessary to repeat the oil process twice or even three times. When the article is cold it may be well polished with a stove brush with the application of a little of the finest graphite that is procurable. Very fine grades of plumbago are supplied by a few firms for electrotyping—an analogous operation. Several methods of procedure may now be adopted :—

I. A lengthy brushing with this blacklead in every detail of the surface may suffice to obtain the needful conductance, but it is not usual to rely on this. There are better conducting substances which may be applied.

II. A thin film of silver sulphide (Ag_2S), which is a good conductor, is obtained in the following way: A solution of silver nitrate in alcohol is applied to the hardened oil surface of the plaster figure and allowed to dry. When dry the article is placed in an air-tight box and a stream of sulphuretted hydrogen passed in. This gas is prepared by placing a few pieces of fused iron

sulphide (FeS) in a bottle, covering with water and adding common hydrochloric acid. Then :—

$$FeS + 2HCl = FeCl_2 + H_2S$$

The bottle may be placed in the box, and the gas coming into contact with the silver nitrate on the figure converts it to silver sulphide, thus :—

$$2AgNO_3 + H_2S = Ag_2S + 2HNO_3$$

The figure is rinsed and wired ready for immersion in the plating solution. Wiring is a matter which will need a little thought. It would be well if the wire leading in the current could touch the article at several points, and these points should, if possible, be obscure ones in which there would ordinarily be greater difficulty in deposition, and, moreover, less obvious defects due to contact of the wires.

After wiring, the work may be immersed in a plating bath. Plaster will require sinking, and this can be done by means of a piece of lead tied on with string. The safest procedure is to first deposit a coat of copper in the acid sulphate bath (see page 101). The deposition should proceed slowly in order to maintain a smooth deposit which can be thickened at will. This deposit may now be smoothed up and scratch-brushed and is available for coloring, or it may receive a further deposit of silver and be subsequently colored.

III. An alternative method of rendering the surface conductive is to apply to it an alcoholic solution of orange shellac mixed with a little Venice turpentine. This mixture is painted on and allowed to dry. While the varnish is still tacky, fine copper bronze powder is applied

by means of a soft brush until the surface is completely covered. After complete drying and hardening, any loose powder is detached and, after wiring, the work is ready for the plating bath.

If these processes are applied with care, very good imitations of a real bronze may be made. There are many good works of art in plaster, and still more value could be placed on such goods if, after the newness of the plaster has gone, they could be sheathed in metal and colored variously to imitate a bronze.

Treatment of Wood.—Wood can be treated similarly. It must first be made impervious to solutions. This may be done in several ways :—

1. The wood may be varnished and allowed to dry.
2. It may be treated with oil, as in the case of plaster, or,
3. It may be treated with paraffin wax, so that by playing a small flame over it the wax is melted and absorbed in the pores of the wood. When one or other of these processes has been successfully applied, metallisation and plating follow on lines similar to those in the case of plaster.

Filling in Letters and Figures with Wax.—The metal colorer may have from time to time to deal with work with cut letters or figures which may need renewal by filling in with wax.

To do this the old and perished wax must first be carefully cleaned out, taking care not to damage the sharp edges of the lettering. The plate or other work is then warmed in a stove or on a hot plate and sealing-wax of the desired color is melted into the required spaces up to the level of the surface. A glass, agate or bloodstone burnisher is moistened on an oil pad, and while the wax

is still warm it is pressed smoothly between the letters by means of the burnisher. In this operation the sharp edges of the letters should cut away superfluous wax by the pressure of the burnisher. Ragged edges must not be left. These can be cut away by a warmed knife moistened with oil to prevent the sticking of the wax. When quite cold the work is finished by coloring or polishing as may be necessary owing to the slight smearing of the wax. Ordinarily the work has been finished and colored prior to filling in with wax.

Filling in with Colored Enamels.—Colored enamels are also used in the filling-in process, after the work is finished and lacquered. The enamel of the required color is now applied by means of a suitable brush, taking care not to overrun the margin of the letters. Should such overrunning occur, the excess enamel may be removed by wiping with a soft rag moistened with a mixture of equal parts of turpentine and linseed oil. This may be conveniently done by covering the first two fingers with "finger stalls." Finger No. 1 is then used for removing the superfluous enamel after dipping into the turpentine and oil mixture, and this is followed by a little polishing effected by finger No. 2. In course of time the finger stall of No. 2 is transferred to finger No. 1 and a new one put on No. 2. Finally, warm the work on a hot plate to 100° F. for about half an hour to dry and harden the enamel before handling.

Yellowish Green Verde.—A yellowish green verde shade can be produced as follows: Copper plate the article in the suitable solution and obtain a fairly stout deposit. Finish by scratch-brushing or obtain any other desired finish. Color to a dark brown shade, approaching black,

in any of the usual solutions containing potassium sulphide, ammonium sulphide or barium sulphide. Rinse in cold water then in hot and dry off in sawdust. Dry scratch-brush. Prepare the following solution :—

Copper nitrate . .	2 ozs.	12½ grms.
Sal ammoniac . .	2 ,,	12½ ,,
Calcium chloride . .	2 ,,	12½ ,,
Water	1 gal.	1 litre

Pass the work through the thoroughly mixed solution, or apply with a brush and allow to drain. Before quite dry stipple all over with a brush and thus obtain a good effect. After stippling, it may be necessary to give the work an immersion in clean cold water and allow it to dry. If a satisfactory effect has been obtained, the work is finished with a brush lubricated with beeswax to give a fine wax finish.

Electro-metallic Decorations.—These are applied to articles which may be of paper pulp, wood, plaster or wood pulp, generally plain in character. A design is neatly carved upon the surface to a depth of about $\frac{1}{32}$ in. If the article is of wood it should first be varnished all over with shellac varnish, or a good copal varnish, and allowed to dry hard. The design is then carved, and at the bottom of the groove a few pins from $\frac{1}{4}$ in. to $\frac{1}{2}$ in. long partially driven in. Fine wire, say 36 gauge, is then wound round the pins, which are then driven home, and thus a continuous metallic connection is made along the bottom of the carved groove. The ends of the wire are then connected together and the finest grade of blacklead well rubbed with a soft brush into the design, so that there will be a conducting surface over the area of the

groove. Any excess of blacklead is washed away and the article weighted with a piece of lead attached with string (not wire) and suspended as a cathode in the acid copper bath (see page 101). With the application of the current, copper is at once deposited upon the wire and upon the blackleaded groove. This may be allowed to continue, having due regard to the rate of deposition to avoid a powdery deposit, until the groove is filled with copper. The article is rinsed and dried slowly, and when dry the deposited copper can be burnished or polished. The work is finished by varnishing all over.

Plaster work must be saturated with boiled linseed oil and dried and baked in an oven after the design has been cut. Very fine holes are then drilled at the bottom of the groove into which the pins fastening down the connecting wires will be subsequently forced. These pins may be of copper or lead, and tin-foil may in this and in the previous case be substituted for copper wire. Blackleading and copper deposition then proceed as before.

Such work lends itself to still further embellishment by the use of spray lacquers and enamels.

In addition, other methods may be used for the deposition of the copper on the nonconducting groove. These methods have already been described on page 233.

A Good Brush Sand Finish.—A very effective half-lustre finish may be produced on metals by the use of French sand and a fine crimped brass wire scratch brush. The sand is fed with water on to the work as the scratch brush revolves, and French sand is suitable because it flows freely with the water, thus giving a better finish than pumice, which is likely to give a streaky finish. This half-lustre finish may be put on the high lights, while the

low lights may be blackened in with a black lacquer which may be dead or bright as required for contrast. This black lacquer is applied after the high lights have been lacquered. Alternatively other shades of lacquer may be used in place of the black as taste may suggest. If in filling in the low lights some of the lacquer exceeds the limits, any excess may be removed by wiping with a soft rag moistened with a mixture of equal parts of turpentine and linseed oil, which will not injure the lacquer on the high lights.

French sand may usually be obtained from a brass foundry.

Copal Finish on Metals.—A satisfactory finish on metal articles may be obtained by a coating of good copal varnish evenly applied with a good fitch-hair brush. When well covered with the varnish and free from air bubbles and dust, the work is stoved or heated on a hot plate at 80° F. for 40 minutes, or longer in the case of large work. It is then removed from the stove or hot plate without handling and allowed to cool. It will then withstand considerable wear.

For a deep gold shade the work should be first coppered, finishing with a good pink shade, and, after the usual drying out, should be finally and completely dried by warming to 100° F. The copal varnish is then applied as above and stoved on the hot plate until a pleasing deep gold shade is obtained. It is then removed from the hot plate and allowed to cool prior to handling.

Variations of the shade are possible. A somewhat higher temperature and longer heating will vary the shade to dark brown on copper. On brass other effects can be produced, while on silver a pale gold is easily obtained.

On a steel bronze the color will vary from brown to a deep chocolate. On "copper ox" the colors are from greenish shades of a dark hue to dark brown. The operator will find the possibility of still greater variations, governed somewhat by the color of the base. One of the chief factors is the control of the temperature. If this is too high or too suddenly applied, the varnish will be burnt and unsightly. Where a quantity of work is being treated, an enamelling stove may be used with a thermometer to indicate the temperature. To maintain the finish, articles, after dusting, should from time to time be wiped with a slightly oiled cloth.

Filling in Lettering on Engraved Plates by the Eastern Method.—In Eastern countries the following method is used. The metals, silver, copper and lead, are melted together in the proportion of 1, 5 and 7 parts by weight with 5 parts by weight of sal ammoniac. The resulting alloy is poured into a crucible containing a paste of powdered sulphur and water. The crucible is then closed to prevent the access of air and is heated over a fire to expel excess of sulphur. The resulting mixture of sulphides is coarsely ground and mixed to a paste with sal ammoniac solution and rubbed into the engraving. The plate is then heated in a muffle until the compound in the engraving melts and adheres to the metal. The plate is cooled, moistened with the chloride solution and again heated to dull redness, after which the engraved surface may be smoothed and polished without fear of the black compound dropping out. The method is specially recommended for solid silver plates.

CHAPTER XX

GENERAL REPAIRS

Repairs to Work.—The electroplater and metal colorer is often confronted with the task of handling work of a very flimsy nature with the consequent risk of breakage. To him it is an asset to be able to effect a quick and neat repair, as much time may be lost in putting the work out. A few large firms will, of course, have their own shops for general repairs, but in many smaller concerns a home repair, if executed satisfactorily, will be of considerable advantage, and the experience of one of the authors may be of service.

Soft Soldering Zinc Alloys.—A large amount of work consists of zinc or zinc alloys. These are brittle metals, especially in the case of old work, and need very careful handling. In a case in mind, a small statue about 4 ft. high came into the shop to be colored Florentine bronze and repaired. The figure was of an Arab boy holding a lamp above the head. Some of the fingers were missing. The metal—a zinc composition—broke with a fracture resembling badly burnt clay, the rough points of the fracture being easily rubbed off. Soldering was tried for some of the parts, but with very little handling these broke away again. Some fingers were fashioned from lead, but these could not be satisfactorily soldered. In the end the job was sent to a firm of repute for repair, but when returned and unpacked, some of the parts were still

broken, and it was evident that attempts had been made to effect the repairs but they had been quite unsuccessful. It was the author's determination that the work should be done, and satisfactorily too, and that the figure should be returned complete and with the required bronze.

To achieve this, all fractures were filed clean and a V-shaped groove made through one-third of the thickness. A flux compound of zinc chloride, sal ammoniac and tin was laid on the prepared surface and allowed to stand for five minutes before applying the solder. Each half of the joint was then tinned, using a large and hot soldering-iron. A good temperature is required to fuse the alloy with the solder without fusing any part of the alloy frame. Having tinned the two surfaces to be joined, they were placed together in position and secured temporarily with wire. The surfaces were moistened with flux and solder applied from a thin stick of the metal until the V-groove was filled level with the adjacent metal, working the soldering-iron from side to side of the groove. The solder quickly set, and the joints thus made were the strongest parts of the work. The joints were then smoothed down with emery cloth and finished with a burnisher. The figure was then coppered and satisfactorily bronzed.

Britannia Metal.—Another case which bears recital was that of a B.M. teapot which, during polishing, suffered a collapse and became holed to about 2 ins. in diameter. Twenty to thirty years ago these were common workshop thrills. For repair, the following course was adopted. The edges of the hole were neatly trimmed with a knife and an outline of the hole was taken by rubbing the edges with a soft lead pencil and pressing a piece of smooth paper against it. This served

as a pattern from which a piece of sheet lead was cut to size and the edge hammered thin and scraped clean. Next, the edges of the hole and of the patch were trimmed. This was not an easy task, but was, nevertheless, effected with soft solder. A piece of tinned iron 6 ins. long and $\frac{1}{2}$ in. wide was bent to form a V-shaped gutter along its length. Solder was melted into this groove. The lead patch was placed on the bench and the edge covered with finely powdered resin. The end of the V-groove was placed at a point on the edge of the patch and the soldering-iron applied to the solder in the groove, the groove being moved slowly round the edge of the patch as the solder ran from the groove. This enabled the solder to unite with the lead without melting the lead. To deal similarly with the edge of the hole was a still more delicate and difficult task. The same V-groove was used and the outside edge of the hole was thus " tinned." The tinned edges of both patch and hole were smoothed, and the patch was supported in position from the inside by some convenient method of packing such, for example, as a stuffing of cloth. Powdered resin was then applied and jointing accomplished by the further use of the V-groove, this being used in each case to avoid any risk of touching either the lead of the patch or metal of the pot with the hot iron. Thus was the patch fixed in position and surplus solder was removed by filing and by emery cloth. Any similar job would now be tested for leaks, and, if found satisfactory, the work is passed forward for plating. On the finished article it should be impossible to easily detect where such a patch has been added, but much depends upon the skilful use of the soldering-iron and V-groove.

"German Silver."—Metallurgists rightly prefer to call this alloy nickel brass, it being an example of a low copper brass in which a part of the zinc is replaced by nickel. The alloy is much used in the electroplate trade.

An experience with an oval dish of this metal with a beaded edge of soft metal may be recounted. The dish had been placed too near a fire and a part of the beaded edge had melted away. The repair was effected by first taking a mould in plaster of Paris of a perfect part of the beading. The mould was thoroughly dried and black-leaded to ensure the separation of a lead cast which was subsequently made. This cast was trimmed to size, soldered in position and " doctor " silvered. An excellent repair was thus made.

Such brief descriptions of actual cases of difficult repairs which were satisfactorily performed may be helpful to others in isolated workshops, if only as suggestive of means by which other similar jobs may be tackled.

Hard Soldering. Brazing.—For soldering silver, brass, copper and all hard metals which are usually joined by a metal of high fusing-point, a blowpipe is an essential tool. Take, for example, the case of joining two pieces of ordinary wrought iron. The edges are filed clean to a width of about an inch and shaped so that when pressed together they make a good fit. A thin strip or wire of good pale yellow brass (say 66 copper to 34 zinc) is secured. This will melt at about 950° C. The pieces of metal to be brazed are now mounted on a fire-brick and packed into position by means of crushed asbestos or similar refractory material. The parts to be brazed are left exposed and then covered with a layer of borax, a vessel of this material being kept close at hand.

The blowpipe flame is now played upon the exposed metal to be joined, and when this acquires a nearly white heat the brass strip or wire is held close to the iron joint in the flame. The brass melts and runs evenly along the joint. The work is cooled and excess of metal filed off. The finished job will show very little trace of the brazing solder applied. This example will provide a guide to jobs of a similar character.

Silver Soldering.—Silver solders are hard alloys containing a sufficient proportion of silver to produce silver whiteness. Some compositions are given below. The operation is very similar to that of brazing. As an experiment a piece of brass wire may be taken and formed into a ring, triangle or other shape so that the ends meet quite flush and are clean. This is placed on a firebrick, or on charcoal, and the ring or other work supported so that the two ends to be joined are quite flat. To do this a cavity may be scooped out of the charcoal and the ring supported vertically, the part to be joined resting on the cavity. The intended joint is covered with a little borax paste and a small piece of silver solder cut and placed upon it. The blowpipe flame is now applied, directing the fine point of the flame on to the silver solder until it runs well into the ring joint. The flame is then withdrawn and the job cooled and pickled in sulphuric acid (1–10 water). This removes the fused borax. The ordinary mouth blowpipe should be used for such small work.

For hard soldering silver, jewellers use a solder containing silver 19 parts, copper 1 part and brass 1 part. Some practice is necessary in order to acquire the skill essential to a good job, and this may easily be obtained

on odd pieces of silver. In any case practice must be accompanied with patience.

Solders and their Composition.

Solder.	Composition.	Flux.
Gold Solder	Gold 12, Silver 2, Copper 4	Borax
Silver Solder ordinary (1)	Silver 19, Copper 1, Brass 1	,,
,, ,, ,, (2)	Silver 2, Brass 1	,,
,, ,, for Brass ..	Silver 1, Brass 1	,,
,, ,, low melting	Silver 1, Brass 1, Zinc 1 ..	,,
Hard Solder for Brass ..	Copper 2, Zinc 1	,,
,, ,, low melting	Copper 1, Zinc 1	,,
Soft Solder ordinary ..	Tin 3, Lead 2	Zinc Chloride or Resin
,, ,, fine	Tin 2, Lead 1	,,
Pewterer's Solder ..	Lead 4, Tin 3, Bismuth 2 ..	,,

Melting-points of Soft Solders.

(1) Tin 3, Lead 2; melting-point 334° F. or 168° C.
(2) Tin 2, Lead 1; ,, ,, 340° F. or 171° C.

Glass Enamel.—It may also come within the requirements of the metal colorer to be able to repair glass enamel ware. The following method will be found serviceable. The enamel is first prepared by melting together crystal glass, borax and metallic oxides.

For a transparent red the following materials are required :—

Purple of Cassius	65 parts
Crystal glass	30 ,,
Borax	4 ,,

The mixture is heated in a crucible to 2000° F., and, when melted, is poured into water to produce a granular enamel. This material is now dried and reduced to a fine powder. It is then mixed with water to a paste and

applied with a steel spatula to the clean surface of the article to be enamelled. The enamel is allowed to dry and then placed in a muffle heated by atmospheric gas burners until the enamel melts and flows evenly. When cold, the article is polished to remove excess of enamel from parts on which it is not required, and the exposed metal surface finished by burnishing.

Various shades may be made, and usually the compositions may be obtained from jewellers' supply stores ready for use.

APPENDICES

I. GLOSSARY OF WORKSHOP TERMS

ANODE. The plate of metal in a plating solution by which the current enters the solution and from which metal dissolves under the influence of the current to maintain the metal content of the solution. The anode isconnected to the positive pole of the generator.

BLINDING. A method by which badly scratched metal may be finished by polishing along the line of the scratches until the surface is bright and the fault becomes less conspicuous.

BLISTER. A term descriptive of badly plated work having a blistered appearance. This is due to a loosening of the deposit which will inevitably strip under the action of the scratch brush or polishing mop.

BOBS. Polishing wheels of solid felt or leather, or wood discs edged with these materials.

BREAKING DOWN. Taking off the edge from a new wire scratch brush by running it against a piece of iron or an old and worn file.

BUFFING. Originally a method of polishing metal with some form of leather. The term is now not largely used.

BURNING. When electro-deposition proceeds too rapidly the metal assumes a granular and non-adherent form, usually at the edges first. Such deposits are said to be " burnt."

BURNISHING. Giving a metal a very high lustre by rubbing with a smooth steel, agate or bloodstone tool called a burnisher. This prepared surface is dense and durable.

CATHODE. In a plating bath the work being plated is the cathode. It receives the deposited metal, and by it the current leaves the solution. It is connected directly or indirectly to the negative pole of the generator.

CLEANING. Preparing goods for electroplating and coloring.

COLORING. Methods by which a fine finish is given to silver, gold and other metals with rouge or prepared lime.

CUTTING DOWN. Diluting a liquid such as solution, varnish or lacquer.

CUTTING DOWN. Grinding down rough surfaces by means of bobs dressed with coarse grades of emery.

CUTTING THROUGH. When the operation of polishing a plated surface is carried too far, thus exposing the underlying metal.

DEAD SURFACE. A dull finish on metal goods without lustre, obtained chemically by special acid treatment or mechanically by sandblasting or scratch-brushing.

DIPPING. The removal of films of tarnish from metal goods by passing through an acid or other liquor.

DOCTORING. Local deposition on patches on which a plated deposit has been cut through (see p. 191).

DRYING OFF. Removing oil or grease from a polished surface by powdered lime or rouge.

DRYING OUT. Removal of moisture from metal goods by means of hot air or hot sawdust.

FAKING. Making good, defective portions of bronzed goods, especially in repair work.

FROSTING. Imparting to a metal a fine grain, sparkling but slightly roughened surface.

GASSING. Occurs on some plating solutions and is due to the evolution of hydrogen at the cathode.

GLAZING. A method of imparting a glassy finish on iron and steel goods by using a hard felt or leather-covered bob.

GRINDING. Using coarse emery on wheels to prepare a surface for finer grades and sanding.

HIGH LIGHTS. The elevated portions of a figured surface.

LOW LIGHTS. The depressed portions of a figured surface.

MATT SURFACE. A dull finish without lustre. Also dead surface.

ORMULU. Term descriptive of special gilt finish on French clocks and other ornamental gilt work.

PARCELLING. The treatment of only a part of a surface by plating or coloring.

PATINA. The color or incrustation which age imparts to metallic works of art.

QUICKING. Imparting a very thin film of mercury to a metal prior to silverplating, by passing the cleaned metal through a mercury solution.

REDUCER. A thinning solution for lacquers.

RELIEVING. Removing the color from high lights by light scratch-brushing or scouring.

RUNS. In lacquering, the local accumulations of lacquer.

STIPPLE. To dot a surface by a succession of dabs with a fairly stiff brush.

STRIP. A solution for removing an old deposit prior to replating.

STRIPPING. Detachment of a deposit from the basic metal. Also process of removing old deposits.

TONING. A process of improving the color on a metal as a final finish.

UNDERCUT. A term descriptive of figured work on which some parts are overhung by others.

VERDE. A term applied to the green incrustation on such metals as copper and brass.

WHITENING. Imparting a thin film of silver by passing metal goods through certain silver solutions without the use of the electric current.

II. GENERAL INFORMATION

Metric System

10 millimetres	=	1 centimetre.
10 centimetres	=	1 decimetre.
10 decimetres	=	1 METRE.
1000 metres	=	1 kilometre.
10 milligrams	=	1 centigram.
10 centigrams	=	1 decigram.
10 decigrams	=	1 GRAM.
1000 grams	=	1 kilogram.
1000 cubic centimetres	=	1 cubic decimetre.
	=	1 LITRE.
1000 litres	=	1 cubic metre.

Conversion Tables

Length.

1 inch	=	2·54 centimetres.
1 foot	=	0·3048 metre.
1 yard	=	0·9144 metre.
1 mile	=	1·58 kilometres.

Area.

1 sq. inch	=	6·45 sq. cms.
1 sq. foot	=	9·28 sq. dms.

Mass or Weight.

15·432 grains	=	1 gram.
1 pound (av.)	=	453·6 grams.
1 ounce (av.)	=	28·4 grams.
1 ounce (troy)	=	31·1 grams.
2·204 lbs. (av.)	=	1 kilogram.

Volume.

1 pint (20 fl. ozs.)	=	567 cubic centimetres.
1 fl. oz.	=	28·4 c.c.
1 gallon	=	4·536 litres.
1·76 pints	=	1 litre.
1 cu. ft.	=	28·4 litres.

Strength of solution.

1 lb. per gall. = 100 gms. per litre.

Hence :—

ozs. per gall. $\times 6\frac{1}{4}$ = gms. per litre.

lbs. per gall. $\times$ 100 = gms. per litre.

grains per gall. are parts per 70,000

$$\therefore \frac{\text{grains per gall.}}{70} = \text{gms. per litre.}$$

Electrical Quantities.

1 coulomb = 1 ampere second and deposits
·000329 gram Cu or
·001118 gram Ag.

1 ampere deposits 1·182 gm. Cu per hour.

1 ampere deposits 4·024 gm. Ag per hour.

1 ampere hour = 3600 coulombs.

96,540 coulombs or 26·8 amp. hrs. } deposit one gram equivalent of any metal.

1 watt = 1 volt ampere.

1 horse-power = 746 watts.

1 kilowatt hour = 1000 watt hours = 1 Board of Trade Unit (B.O.T.U.) = $1\frac{1}{3}$ horse-power hours.

TABLE II

SPECIFIC GRAVITY OF SULPHURIC ACID SOLUTIONS AT 15° C.

Specific gravity.	Percentage of H_2SO_4.	Specific gravity.	Percentage of H_2SO_4.
1·0064	1	1·306	40
1·013	2	1·351	45
1·019	3	1·398	50
1·0256	4	1·448	55
1·032	5	1·501	60
1·039	6	1·557	65
1·0536	8	1·615	70
1·068	10	1·675	75
1·083	12	1·734	80
1·114	16	1·786	85
1·144	20	1·822	90
1·182	25	1·8376	95
1·223	30	1·8426	100
1·264	35		

TABLE III

SPECIFIC GRAVITY OF HYDROCHLORIC ACID SOLUTIONS

Specific gravity.	Percentage of HCl.	Specific gravity.	Percentage of HCl.
1·200	40·8	1·098	20
1·197	40	1·074	15
1·174	35	1·064	13
1·164	33	1·054	11
1·154	31	1·0437	9
1·141	28·5	1·0318	6·5
1·131	26·5	1·026	5·3
1·118	24·0	1·020	4
1·108	22	1·012	2·5

TABLE IV

SPECIFIC GRAVITY OF NITRIC ACID SOLUTIONS AT 15° C.

Specific Gravity.	Percentage HNO_3.	Specific Gravity.	Percentage HNO_3.
1·530	100	1·304	48
1·516	96	1·284	45
1·509	94	1·264	42
1·495	90	1·251	40
1·478	85	1·225	36
1·470	83	1·198	32
1·460	80	1·185	30
1·442	75	1·172	28
1·423	70	1·138	23
1·405	66	1·120	20
1·395	64	1·089	15
1·386	62	1·077	13
1·374	60	1·067	11·4
1·346	55	1·045	7·2
1·335	53	1·022	4·0
1·317	50	1·010	2·0

TABLE V

SPECIFIC GRAVITY OF AMMONIA SOLUTIONS AT 14° C.

Specific Gravity.	Percentage of NH_3.	Specific Gravity.	Percentage of NH_3.
0·996	1	0·9414	15
0·987	3	0·925	20
0·979	5	0·911	25
0·971	7	0·898	30
0·959	10	0·886	35
0·952	12	0·880	36

TABLE VI

THERMOMETRIC SCALES

°C.	°F.	°C.	°F.
0	32	55	131
5	41	60	140
10	50	65	149
15	59	70	158
20	68	75	167
25	77	80	176
30	86	85	185
35	95	90	194
40	104	95	203
45	113	100	212
50	122		

To convert ° C. into ° F. :—

Multiply by $\frac{9}{5}$ and add 32.

Thus :—

$$50\ ^\circ\text{C.} = \left(50 \times \frac{9}{5}\right) + 32 = 122^\circ\ \text{F.}$$

To convert ° F. to ° C. :—

Subtract 32 and then multiply by $\frac{5}{9}$

Thus :—

$$185^\circ\ \text{F.} = (185 - 32) \times \frac{5}{9}$$

$$= 153 \times \frac{5}{9} = 85^\circ\ \text{C.}$$

TABLE VII

COMMON AND CHEMICAL NAMES AND FORMULÆ OF SUBSTANCES

Common Name.	Chemical Name.	Formula.
Oil of vitriol	Sulphuric acid	H_2SO_4
Aqua fortis, Ackey	Nitric acid	HNO_3
Spirits of salts, Muriatic acid	Hydrochloric acid	HCl
Vinegar	Acetic acid	$H{\cdot}C_2H_3O_2$
Caustic potash	Potassium hydroxide	KOH
Caustic soda	Sodium hydroxide	NaOH
Quicklime	Calcium oxide	CaO
Caustic lime, Slaked lime	Calcium hydroxide	$Ca(OH)_2$
Soda ash	Dry sodium carbonate	Na_2CO_3
Washing soda	Cryst. sodium carbonate	$Na_2CO_3 10H_2O$
Bicarbonate of soda	Sodium hydrogen carbonate	$NaHCO_3$
Chalk, Whiting	Calcium carbonate	$CaCO_3$
Spirits of hartshorn, Liquor ammonia	Ammonium hydroxide	NH_4OH
Bluestone or Blue vitriol	Copper sulphate (crystalline)	$CuSO_4{\cdot}5H_2O$
White vitriol	Cryst. zinc sulphate	$ZnSO_4{\cdot}7H_2O$
Green vitriol	Cryst. ferrous sulphate	$FeSO_4{\cdot}7H_2O$
Glauber salt	Sodium sulphate	$Na_2SO_4{\cdot}10H_2O$
Epsom salt	Magnesium sulphate	$MgSO_4{\cdot}7H_2O$
Single nickel salt	Nickel sulphate	$NiSO_4{\cdot}7H_2O$
Double nickel salt	Nickel ammonium sulphate	$NiSO_4{\cdot}(NH_4)_2SO_4{\cdot}6H_2O$
Common salt	Sodium chloride	NaCl
Sal-ammoniac	Ammonium chloride	NH_4Cl
Corrosive sublimate	Mercuric chloride	$HgCl_2$
Nitre or Saltpetre	Potassium nitrate	KNO_3
Chili saltpetre	Sodium nitrate	$NaNO_3$
Lunar caustic	Silver nitrate	$AgNO_3$
Liver of sulphur	Potassium sulphide	K_2S
Brimstone	Sulphur	S

TABLE VII—*contd.*

Common Name.	Chemical Name.	Formula.
Barium sulphuret	Barium sulphide	BaS
Stibnite	Antimony sulphide	Sb_2S_3
Sulphuret of ammonia	Ammonium sulphide	NH_4HS
Sugar of lead	Lead acetate	$Pb(C_2H_3O_2)_2 \cdot 3H_2O$
"Hypo"	Sodium thiosulphate	$Na_2S_2O_3 \cdot 5H_2O$
White arsenic	Arsenious oxide	As_2O_3
Cream of tartar Argol	Potassium hydrogen tartrate	$KHC_4H_4O_6$
Borax	Sodium biborate	$Na_2B_4O_7$
Spirits of wine	Ethyl alcohol	C_2H_6O
Ether Sulphuric ether	Diethyl ether	$C_4H_{10}O$
Crocus Rouge	Ferric oxide	Fe_2O_3

TABLE VIII

TWADDELL HYDROMETER SCALE

Degrees Twaddell.	Sp. Gr.	Degrees Twaddell.	Sp. Gr.
0	1·000	60	1·300
1	1·005	70	1·350
2	1·010	80	1·400
3	1·015	90	1·450
4	1·020	100	1·500
5	1·025	110	1·550
10	1·050	120	1·600
20	1·100	130	1·650
30	1·150	140	1·700
40	1·200	150	1·750
50	1·250	160	1·800

$$\text{Specific gravity} = \frac{\text{Degrees Twaddell} \times 5}{1000} + 1$$

$$\text{Degrees Twaddell} = (\text{Specific Gravity} - 1) \times 200$$

TABLE IX

Beaume Hydrometer Scales

°B.	Sp. Gr.		°B.	Sp. Gr.	
	Heavier than Water.	Lighter than Water.		Heavier than Water.	Lighter than Water.
0	1·000	—	18	1·143	0·948
1	1·007	—	19	1·152	0·941
2	1·014	—	20	1·161	0·935
3	1·021	—	21	1·170	0·929
4	1·029	—	22	1·180	0·922
5	1·036	—	23	1·191	0·917
6	1·043	—	24	1·200	0·911
7	1·051	—	25	1·211	0·907
8	1·059	—	26	1·220	0·900
9	1·067	—	27	1·231	0·895
10	1·075	1·000	28	1·242	0·889
11	1·083	0·993	29	1·252	0·884
12	1·091	0·986	30	1·263	0·878
13	1·099	0·980	40	1·385	0·828
14	1·108	0·973	50	1·532	0·783
15	1·116	0·967	60	1·714	0·742
16	1·126	0·960	70	1·946	0·706
17	1·134	0·954	75	2·087	0·689

Liquids heavier than water :—

$$\text{Sp. gr.} = \frac{144}{144 - \text{degrees Beaume}}$$

Liquids lighter than water :—

$$\text{Sp. gr.} = \frac{144}{134 + \text{degrees Beaume.}}$$

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